Base metal recovery from glycine leach solutions using ion exchange or solvent extraction

by

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DECLARATION

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ABSTRACT

Technological advances lead to a reduced life span of electronic equipment. This leads to large quantities of electronic waste being produced. The recovery of metals from electronic waste has both an environmental and economical drive. Various hydrometallurgical routes have been proposed for this purpose, but most of them use multiple lixiviants for base and precious metal leaching stages. Glycine in alkaline solutions has been proposed as an alternative lixiviant as it can leach both base and precious metals at varying operating conditions. This reduces the need for washing stages between leaching steps and thus the loss of reagents. Limited research has been done on the recovery of copper from these glycine pregnant leach solutions (PLS). This study investigates the use of solvent extraction or ion exchange to isolate and concentrate copper from the glycine PLS.

The primary objectives of the study included to investigate the effect of key operating variable such as pH, reagent concentration and extractant functional group on the recovery of copper. A flowsheet was developed for the isolation and concentration of copper from the glycine PLS using solvent extraction.

A synthetic PLS was produced which contained 10g/L copper, 1.5g/L lead and 1.1g/L zinc. pH values ranging from 8 to 11 were evaluated and solvent concentrations between 5 and 20%. LIX-84I was found to be highly selective for copper at the conditions tested. No co-extraction of any other metals was found. Increasing the pH of the aqueous phase improved the recovery of copper from 64 to 86% in a single stage with a 20% solution of LIX-84I. Increasing the solvent concentration from 5 to 20% at a pH of 10 showed an almost linear increase in the recovery from 17% with a 5% LIX-84I concentration to 64% with a 20% LIX-84I concentration. Equilibrium isotherms were drawn for 5, 10 and 20% LIX-84I concentrations and showed that 80% copper recovery is possible with 2 stages from a PLS containing 10g/L of copper at a A:O ratio of 2:1. 2M sulphuric acid can successfully strip 100% of the copper from a loaded organic phase with O:A ratios of up to 4:1, resulting in a final copper concentration of 27g/L in the concentrated electrolyte. The fate of glycine during the solvent extraction was tested using UV-VIS and it was confirmed that no glycine was co-extracted to the organic phase.

Copper recovery from glycine leach liquors was proven to be ineffective using commercially available ion exchangers. Both the iminodiacetic acid resins tested, S930Plus and TP207, showed no selectivity for copper over lead or zinc at the conditions that were tested. The

separation factors found were 0.03 and 0.02 for copper over lead and zinc respectively with S930Plus, for TP207 the values were 0.04 and 0.02 for copper over lead and zinc respectively. S930Plus had equilibrium resin concentration of 11.7g/L copper, 9.1g/L lead and 6.7g/L zinc, and TP207 showed equilibrium concentrations of 16.1g/L copper, 10.5g/L lead and 7.8g/L zinc. Column elution tests showed that all the metals are removed at a similar rate indicating that split elution would not be an option for the purification of copper. The concentrations found in the eluate were 5.5g/L copper, 4.7g/L lead and 3.2g/L zinc from S930Plus and 8g/L copper, 6.2/L lead and 5.2g/L zinc from TP207. The bis-picolylamine resin tested, TP220, showed separation factors of 1.67 and 1.40 for copper over lead and zinc respectively, these values are relatively close to 1 and effective separation of the metals was not achieved, the equilibrium concentrations were, 6.1g/L for copper, 0.9g/L lead and 0.8g/L zinc.

OPSOMMING

Die vinnige tempo waarteen tegnologie ontwikkel veroorsaak dat die lewensduur van elektroniese toerusting aansienlik afgeneem het. Dit lei tot groot hoeveelhede elektroniese afval wat geproduseer word. Herwinning van metale van elektroniese afval bied voordele uit 'n omgewingsimpak sowel as ekonomiese oogpunt. Verskeie hidrometallurgiese roetes is voorgestel vir die behandeling van elektroniese afvanl, maar die meerderheid gebruik veelvuldige logingsmiddels om basis- en edelmetale te loog. Glisien in alkaliese oplossings is voorgestel as 'n alternatiewe logingsmiddel aangesien dit beide basis- en edelmetale kan loog by verskillende toestande. Dit elimineer die vereiste wasprosesse tussen logings en die gepaardgaande verlies van reagense. Daar is nog nie voldoende navorsing gedoen op die herwinning van koper uit glisien logingsoplossings nie. Die huidige studie ondersoek die gebruik van vloeistof-vloeistof ekstraksie en ioon uitruiling om koper te isoleer en konsentreer uit glisien loginsoplossings.

Die hoof doelwitte van die studie was om die effek van sleutel veranderlikes soos pH, reagens konsentrasie en funksionele groep op die herwinning van koper uit die logingsoplossings te ondersoek. 'n Vloeidiagram vir die herwinning van koper met behulp van vloeistof-vloeistof ekstraksie is ook ontwikkel.

'n Sintetiese logingsoplossing met 10g/L koper, 1.5g/L lood en 1.1g/L sink is geproduseer vir eksperimentele toetswerk. pH waardes tussen 8 tot 11 is ondersoek tesame met LIX-84I ekstraheermiddel konsentrasies tussen 5 en 20%. LIX-84I was hoogs selektief vir koper by alle toestande wat getoets is. Geen mede-ekstraksie van enige ander metaal is gevind nie. Verhoging van die pH waardes het gelei tot hoër ekstraksie van koper; die ekstraksie het toegeneem van 64% tot 86% in 'n enkele ekstraksie stadium met 'n toename in pH waardes van 10 tot 11. Ekstraksie het van 17% na 64% toegeneem met die verhoging van die ekstraheermiddel konsentrasie van 5 na 20%. Ewewig isoterme is ontwikkel vir 5, 10 en 20% LIX-84I konsentrasies en dit het gewys dat 80% van die koper in 'n 10 g/L Cu oplossing herwin kon word in 2 ewewigstadia by 'n waterige tot organiese verhouding van 2:1. Alle koper kan in 'n enkele stadium uit die organiese fase verwyder word met 2 M H_2SO_4 by 'n waterige tot organiese verhouding van 1:4; dit gee aanleiding tot 'n finale koper konsentrasie van 27 g/L in die gekonsentreerde elektrolitiese oplossing. Die glisien in die waterige oplossing word nie geëkstraheer deur LIX-84I nie;dit is bevestig met behulp van 'n ninhidrien toets.

Koper herwinning met behulp van ioon-uitruiling was nie effektief nie. Beide iminodiasetiese suur (IDS) harse, naamlik S930 en TP207, het geen selektiwiteit vir koper oor die ander metale gewys nie. Die skeidingsfaktore was 0.03 en 0.02 vir koper oor lood en sink, onderskeidelik, vir S930, en 0.04 en 0.02 vir lood en sink met TP207. S930 het ’n ewewigskonsentrasie van 11.7 g/L getoon vir koper, 9.1 g/L vir lood en 6.7 g/L vir sink. TP207 se ewewigskonsentrasies was 16.1 g/L vir koper, 10.5 g/L vir lood en 7.8 g/L vir sink. Kolomtoetse het gewys dat alle metale teen dieselfde spoed van die harse verwyder word wat toon dat selektiewe verwydering nie ’n opsie is nie. Die hoogste konsentrasies wat gevind was in die finale suuroplossing was 5.5g/L vir koper, 4.7g/L vir lood en 3.2g/L vir sink met S930, en 8g/L vir koper, 6.2g/L vir lood en 5.2g/L vir sink met TP207. TP220, wat ’n bis-pikolielamien hars is, het skeidingsfaktore van 1.67 en 1.40 vir koper oor lood en sink, onderskeidelik, getoon. Die waardes is naby aan 1 wat toon dat geen onderskeid gemaak word deur die hars vir verskillende metale nie. Die ewewigskonsentrasies op die hars was 6.1g/L vir koper, 0.9g/L vir lood en 0.8g/L vir sink.

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NOMENCALTURE

Symbol	Description	Unit
pKa	acid dissociation constant	-
A:O	Aqueous to organic ratio	-
I^- or I^+	Ion exchanger anion or cation	-
Me^{2+}	Metal cation	-
IDA	Iminodiacetic acid	-
Bis-PA	Bis-picolylamine	-
x_s	Subscript referring to solution	-
x_r	Subscript referring to resin	-
x^s	Superscript referring to surface of resin	-
k_s	Mass transfer coefficient between solution and resin surface	-
k_r	Mass transfer coefficient of diffusion onto resin	-
K	Kinetic rate constant	$\frac{L}{g \cdot h}$
q_e	Equilibrium loading on resin	$\frac{g}{L}$
q_t	Current loading on resin	$\frac{g}{L}$
R^+	Organic extractant	-
D_A	Distribution coefficient	-
β_B^A	Separation factor of a over b	-
$\overline{C_A}$	Organic phase equilibrium concentration	$\frac{g}{L}$
C_A	Aqueous phase equilibrium concentration	$\frac{g}{L}$
C_{A0}	Aqueous phase initial concentration	$\frac{g}{L}$
$\%E_A$	Percentage extraction of A	-

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1 INTRODUCTION

1.1 Motivation

The usage of electronic devices in both the private and industrial sector is continuously increasing due to rapid technological development. This has led to a decreased service life and an increased rate of electronic waste (e-waste) generation. Printed circuit boards (PCBs), which make up a large portion of e-waste, contain up to 40% metals by weight. The recovery of these metals can have both environmental and economical advantages (Cui & Forssberg, 2003).

PCBs contain about 150-350 kg of copper per ton of scrap and around 80-500 g/ton of gold; this is considerably higher than in the average ore containing these metals (Ogunniyi, Vermaak & Groot, 2009). Both pyrometallurgical and hydrometallurgical processes have been developed to recover these metals from electronic waste (Cui & Zhang, 2008). Hydrometallurgical processes have the advantages of being less energy intensive, more suitable to handle low grade ore and have the ability to be run on a smaller scale (Bas, Deveci & Yazici, 2013).

Oraby & Eksteen (2014) patented a process whereby the copper from copper-gold ore concentrates can be leached with the use of glycine and hydrogen peroxide in an alkaline solution. The same system at elevated temperatures can successfully leach gold and silver from the same ore concentrates. All of the copper present in its metallic form was leached from the ore (Eksteen & Oraby, 2014; Oraby & Eksteen, 2015). Metals on PCBs are mainly found in their metallic form, this would thus enable a single lixiviant at different conditions to leach both copper and gold selectively from e-waste.

Limited research has been done on the recovery of copper from glycine leach liquors while this is an important step for metal recovery from pregnant glycine leach solutions obtained from e-waste leaching facilities. The aim of this research is to recover copper from glycine leach solutions with the use of ion exchange or solvent extraction. The final concentrated product should allow for the production of marketable copper products such as salts by crystallization or copper cathodes by electrowinning.

1.2 Objectives

The following objectives need to be achieved to evaluate the use of ion exchange or solvent extraction for metal recovery from glycine leach solutions:

- Understand the chemistry, complex formation and metal speciation in a glycine leach solution in order to identify and test suitable ion exchange resins and solvents.
- Perform laboratory scale experimental work to understand the influence that process variables like pH, extractant or resins types and metal concentration have on the overall extent and selectivity of copper recovery.
- Propose a flowsheet including design parameters, operating conditions and mass balances that would allow for efficient copper extraction for downstream processing.

1.3 Document outline

This document consists of a literature review that can be found in chapter 2, experimental design and methodology in chapter 3, discussion of results in chapter 4 and a preliminary flowsheet in chapter 5.

The literature review covers the characterization of printed circuit boards, the chemistry of a glycine leaching system and the workings of ion exchange and solvent extraction including a review of previously published work. Screening tests to find suitable exchangers and extractants were performed followed by optimization of the extraction processes in order to develop the flowsheet.

2 LITERATURE REVIEW

2.1 Background

E-waste is made up of a complex mixture of materials including plastics, ceramics and various metals. Yamane et al. (2011) found that PCBs form personal computers contained around 45% metals, 27% plastics and polymers and 28% ceramics by weight while PCBs from cellphones typically contain 63% metals, 13% plastics and polymers and 24% ceramics. Disposing these materials in a landfill or incineration as part municipal solid waste disposal can potentially have serious negative effects on the environment and human health. This can be because of the leaching of toxic chemicals into the ground water supplies and due to the emission of toxic gases into the atmosphere during incineration. While there are more than a 1000 substances that can be found in electronic waste, the main substances that pose serious risks include lead, cadmium, mercury, hexavalent chromium, plastics including polyvinylchloride (PVC), brominated flame retardants, barium, beryllium, other heavy metals and rare earth metals (Kiddee, Naidu & Wong, 2013; Puckett, Byster, Westervelt, Gutierrez, Davis, Hussain, Dutta, Coalition, Network & Smith, 2002).

Substantial research has been done to investigate the chemical composition, including metal composition, of PCBs. Table 2.1 shows the concentrations of metals commonly found on PCBs in weight percentage.

Table 2.1: Printed circuit board metal content in %weight (adapted from (Ogunniyi *et al.*, 2009))

Source:	(a)	(b)	(c)	(d)	(e)	(f)	(g)	average
Cu	20	26.8	10	15.6	22	17.85	23.47	19.4
Al	2	4.7	7	-	–	4.78	1.33	4.0
Pb	2	–	1.2	1.35	1.55	4.19	0.99	1.9
Zn	1	1.5	1.6	0.16	–	2.17	1.51	1.3
Ni	2	0.47	0.85	0.28	0.32	1.63	2.35	1.1
Fe	8	5.3	–	1.4	3.6	2	1.22	3.6
Sn	4	1	–	3.24	2.6	5.28	1.54	2.9
Sb	0.4	0.06	–	–	–	–	–	0.2
Au/ppm	1000	80	280	420	350	350	570	436
Pt/ppm	–	–	–	–	–	4.6	30	17
Ag/ppm	2000	3300	110	1240	–	1300	3301	1875
Pd/ppm	50	–	–	10	–	250	294	151

Data from: (a) (Sum, 1991); (b) (Zhao, Wen, Li & Tao, 2004); (c) (Zhang & Forssberg, 1999); (d) (Kim, Lee, Seo, Park & Sohn, 2004); (e) (Yokoyama & Iji, 1997); (f) (Kogan, 2006); (g) (Ogunniyi *et al.*, 2009).

Pyrometallurgical processes to recover these metals from e-waste include incineration, smelting in a blast or plasma arc furnace, sintering, melting and reactions in a gas phase (Cui & Zhang, 2008; Hoffmann, 1992; Sum, 1991). These processes have been used to recover non-ferrous and precious metals from e-waste for over 30 years.

These methods are generally energy intensive and rely on the presence of precious metals to be economically viable. The precious metal content of electronic waste has been decreasing over the past few years and will continue to decrease. The combustion of PCBs in pyrometallurgical routes furthermore releases large quantities of polybrominated/chlorinated dibenzo-p-dioxins and dibenzofurans because of the fire retardants that are present. These substances are highly toxic and extra operating costs are induced in order to prevent their release into the atmosphere (Cui & Zhang, 2008; Söderström & Marklund, 2002).

Hydrometallurgical processes are considered to be good alternatives as they are easier to control, can handle lower grade ores, can be operated on a smaller scale and carry less environmental concerns. The main steps in hydrometallurgical routes include: size reduction, concentration by dense medium separation or magnetic separation, followed by a base and precious metals leach in acidic or caustic environments. These leach solutions are then purified using precipitation, solvent extraction and ion-exchange methods to isolate and concentrate the

metals of interest. The solutions are subsequently treated in electrowinning, reduction or crystallization processes to recover solid products (Cui & Zhang, 2008; Gloe, Mühl & Knothe, 1990; Ritcey, 2006; Shamsuddin, 1986)

Base metals on PCBs are mostly present in their respective metallic forms and recovery by hydrometallurgical routes is mainly done using inorganic acids like sulphuric acid and nitric acid (Ghosh, Ghosh, Parhi, Mukherjee & Mishra, 2015). Precious metals are usually recovered with the use of cyanide or cyanide alternatives like thiourea or thiosulfate. These cyanide alternatives have slow leaching kinetics and the presence of base metals pose problems as base metals are known to consume the reagent needed for the recovery of precious metals. Glycine has been proposed as a novel alternative lixiviant to leach both base and precious metals at different conditions. Utilisation of a single lixiviant for leaching base and precious metals results in simplified hydrometallurgical routes with minimal requirements for washing stages and reduced reagent consumption by base metals in precious metal leach phases (Oraby & Eksteen, 2014, 2015). Metal recovery processes from electronic waste with glycine would typically consist of an initial base metal leach followed by a precious metal leach.

Sufficient knowledge to isolate and concentrate metals from glycine leach solutions still lacks, as minimal research has been performed on the glycine leach solution. The main impurities found in the leach liquor after a base metal leach from PCBs include lead, zinc and aluminium. This will be discussed in more detail in section 3.1.4. Solvent extraction and ion exchange are commonly used methods in hydrometallurgy for the isolation and concentration of metals from pregnant leach liquors. This study aims to investigate the use of solvent extraction or ion exchange to isolate and concentrate the copper from a glycine pregnant leach solution (PLS) to create a concentrated liquor that can go for solid metal recovery in the form of crystallization or electrowinning.

This chapter discusses the literature necessary so conduct the research, the information discussed include the glycine leach chemistry and the working of ion-exchange and solvent extraction.

2.2 Glycine leach system

A review of published literature on leaching of base metals, specifically copper, using glycine in alkaline solutions was conducted to understand what the effect of key variables are on the leaching performance and complexation of copper with glycine. This was necessary to select appropriate solvents and resins and to determine operating conditions for the creation of a pregnant leach solution to use during experimental work.

2.2.1 Leaching chemistry

Glycine in an aqueous solution can exist in three different forms namely the cationic, zwitterion and anionic form as shown in equation [2.1] (Aksu & Doyle, 2001).

$$\begin{array}{c} pKa_1 = 2.350 \qquad pKa_2 = 9.778 \\ {}^{+}H_3NCH_2COOH \leftrightarrow {}^{+}H_3NCH_2COO^{-} \leftrightarrow H_2NCH_2COO^{-} \\ (H_2L^{+})\ \text{cation} \qquad (HL)\ \text{zwitterion} \qquad (L^{-})\text{anion} \end{array} \qquad [2.1]$$

Equations [2.2] and [2.3] can be written from the definition of acidity constants K_a, with [HGly] representing the zwitterion, $[H_2Gly^{+}]$ the cation and $[Gly^{-}]$ the anion and $K_a = 10^{-pKa}$.

$$K_{a1} = \frac{[H^{+}][HGly]}{[H_2Gly^{+}]} \qquad [2.2]$$

$$K_{a2} = \frac{[H^{+}][Gly^{-}]}{[HGly]} \qquad [2.3]$$

Solving for the concentrations of the respective glycine species and plotting this over a range of pH values gives a distribution diagram as shown in figure 2.1.

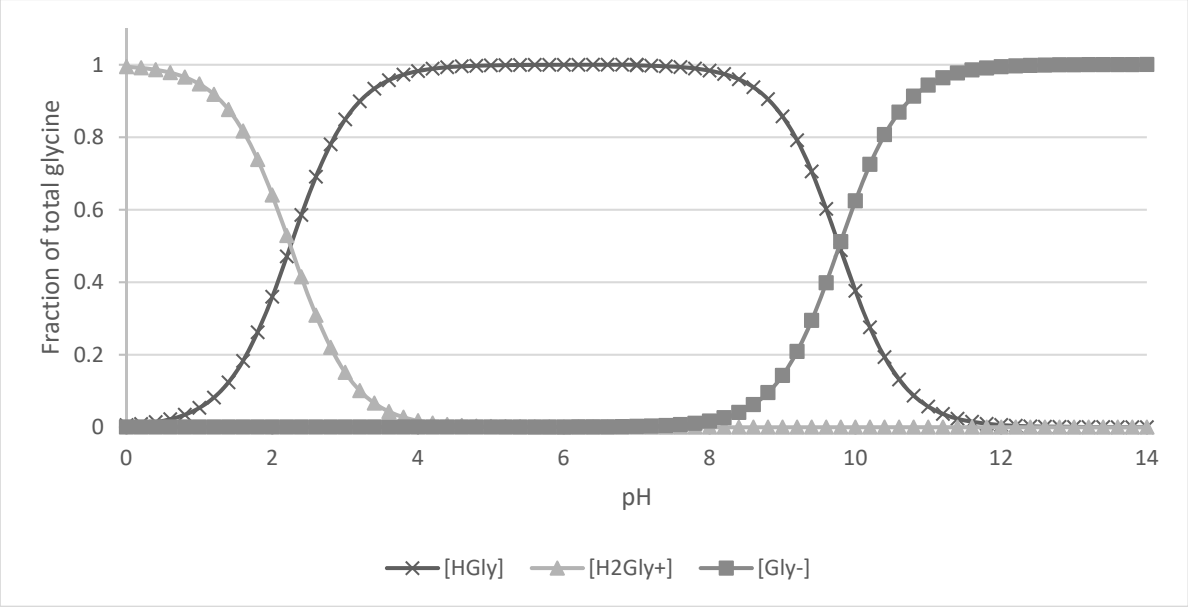

Figure 2.1: Speciation of glycine as a function of pH (adapted from (Lower, 2016))

The cationic form is the most stable at lower pH values as the excess of hydrogen ions in the system will push the reaction as shown in [2.1] to the left. The anionic form is more stable at higher pH values as a result of an increase in the hydroxyle ion concentration. The zwitterion is the predominant species at pH values between the pKa values.

The leaching of copper in a glycine-peroxide system is a two-step mechanism. Initially the copper is oxidized to its cupric or cuprous ions, and this is followed by the formation of a copper-glycine complex (Oraby & Eksteen, 2014; Tanda, 2017). Du et al. (2004) suggest that the reduction reaction in a glycine solution without peroxide can be described as shown in equation [2.4]. Equations [2.5] and [2.6] show the reduction reactions with hydrogen peroxide present. The oxidization of copper takes place as shown in [2.7] and [2.8] for cuprous and cupric ions respectively.

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad [2.4]$$

$$H_2O_2 + 2e^- \leftrightarrow 2OH^- \quad [2.5]$$

$$H_2O_2 + e^- \leftrightarrow OH^{\cdot} + OH^- \quad [2.6]$$

$$Cu \leftrightarrow Cu^+ + e^- \quad [2.7]$$

$$Cu \leftrightarrow Cu^{2+} + 2e^- \quad [2.8]$$

Soluble glycine complexes can be formed with both copper (I) and copper (II). These complexes are as shown in equations [2.9] - [2.11] for copper (II). Equation [2.12] shows the

complexation of copper (I). The stability constants as indicated by Aksu & Doyle (2001) are also shown (Oraby & Eksteen, 2014).

$$Cu^{2+} + H_2NCH_2COO^- \leftrightarrow Cu(H_2NCH_2COO)^+ \qquad \log K = 8.6 \qquad [2.9]$$

$$Cu^{2+} + 2H_2NCH_2COO^- \leftrightarrow Cu(H_2NCH_2COO)_2 \qquad \log K = 15.6 \qquad [2.10]$$

$$Cu^{2+} + {}^+H_3NCH_2COO^- \leftrightarrow Cu(H_3NCH_2COO)^{2+} \qquad \log K = 2.92 \qquad [2.11]$$

$$Cu^+ + 2H_2NCH_2COO^- \leftrightarrow Cu(H_2NCH_2COO)_2^- \qquad \log K = 10.1 \qquad [2.12]$$

The anionic form of glycine will be predominant as pH values of above 10 are used. This will allow the complex formed between the cupric ion and the anionic form of glycine to be the most stable and most present in the leach liquor (Aksu & Doyle, 2001, 2002; Oraby & Eksteen, 2014; Tanda, Eksteen & Oraby, 2017).

The glycine-peroxide system is widely used as a polishing mixture for chemical-mechanical planarization techniques and it shows promising behaviour in the leaching of metallic copper from exposed areas (Aksu & Doyle, 2001; Ein-Eli, Abelev & Starosvetsky, 2004; Oraby & Eksteen, 2014).

Oraby & Eksteen (2014) reported that 98% of copper from a copper-gold concentrate was leached after 48h using 0.3M glycine, 1% hydrogen peroxide, pH 11 at 23°C. The copper was present in a number in copper minerals and some native copper, all of the metallic copper present was leached (Filmer, Parker & Wadley, 1979; Klauber, Parker, van Bronswijk & Watling, 2001; McMillan, MacKinnon & Dutrizac, 1982; Oraby & Eksteen, 2014).

The selectivity of glycine towards copper over other metals like iron and lead was proven to be very good (Oraby & Eksteen, 2014). The final concentration of iron and lead in the first stage pregnant leach liquor were 12mg/L and 16mg/L, respectively, compared to 4745mg/L for copper. The corresponding percentages of metal leaching were 82% extraction for copper, but only 0.06% for iron and 8.5% lead.

2.2.2 Leaching conditions

2.2.2.1 Multiple leaching stages

A two stage leaching process together with single stage leaching was investigated by Oraby & Eksteen (2014) on a mixed gold-copper ore containing 3.75% copper in a range of copper minerals. The two stage leaching was performed using a glycine concentration of 0.3M, 1% hydrogen peroxide, pH 11, pulp density of 16% (%w/v) at 23°C for 48 hours. Almost 80% of

the copper was leached after the first stage with a copper concentration of 4745ppm in the leach liquor. 66% of the copper was leached within the first 5 hours. The rapid initial dissolution of copper is thought to be as a result of the presence of metallic copper and cuprite present in the ore concentrate. An additional 18% of the total copper was leached in the second stage with a resulting copper concentration of 1069ppm in the second leach liquor. This resulted in a 98% overall extraction of copper from the gold-copper ore investigated (Oraby & Eksteen, 2014).

The single stage leaching test was performed using similar conditions, except the glycine concentration was set to 0.4M and 96 hours leaching time. The copper extraction after this single stage leach was found to be 82%. All the metallic copper was leached during this single stage leach (Oraby & Eksteen, 2014).

2.2.2.2 Effect of pH

Tanda (2017) and Oraby & Eksteen (2014) investigated the effect of pH on the leaching of copper in alkaline solutions with the addition of hydrogen peroxide. Tanda (2017) performed test at pH values of 5.8, 8 and 11. The molar glycine to copper ratio was 4:1 and the hydrogen peroxide concentration was set to 0.5%. 0.4% w/v of metallic solids was added with a residence time of 48 hours. Oraby & Eksteen (2014) performed test at pH values of 8, 10 and 11 with 0.3 molar glycine, 1% hydrogen peroxide and 16%w/v concentrated gold-copper ore for 48 hours.

Tanda (2017) found that the amount of copper dissolved increased steadily for the first 24 hours up to a maximum of 55% dissolution at a pH of 5.8, the copper concentration started to decrease thereafter until it reached 30% dissolution after 48 hours.

Both researches found comparable results at a pH of 8 where an initial rapid dissolution of copper was found that reached a maximum of almost 60% after 6 hours. After this it decreased to 26% for Tanda (2017) and to 40% for Oraby & Eksteen (2014) after the 48 hours.

Oraby & Eksteen's (2014) results correspond closely with the results published by Tanda (2017) for pH 10 and 11. The copper dissolution is less rapid initially but steadily increases over time to reach a maximum of over 70% and almost 80% for pH 10 and pH 11 respectively for Oraby & Eksteen (2014) and 92% for Tanda (2017) after 48 hours.

2.2.2.3 Effect of hydrogen peroxide

The effect of hydrogen peroxide addition was studied by adding 0%, 1% and 2% hydrogen peroxide to the leach solution using 0.3M glycine at room temperature. The experiments where run for 48 hours in vented bottles (Oraby & Eksteen, 2014). It was found that the addition of

peroxide did increase the recovery of copper to a certain extend. The recovery of copper without peroxide was 75% while 82% dissolution was found in a 2% peroxide solution. Tanda (2017) performed similar tests using metallic copper in a 4:1 molar glycine to copper ratio at pH 11 and varying the hydrogen peroxide concentrations from 0%, 0.1%, 0.5% to 1%. He found comparable results with faster initial kinetics in the systems where hydroxide was added. N0 significant difference in the amount of copper leached after 48 hours was reported. The final dissolution of copper was 88.8%, 92.2%, 91.7% and 91.2% for initial hydrogen peroxide concentrations of 0, 0.1, 0.5 and 1% respectively.

The reactions shown in equations [2.4]-[2.6] all take place in a system containing hydroxyl ions, thus explaining the higher initial reaction rate in the presence of peroxide as it acts as a very strong oxidizing agent and it increases the concentration of hydroxyl ions. Oraby & Eksteen (2014) and Tanda (2017) however suggests that the reactions with peroxide are fast and only take place in the first 2 hours of the leach as the peroxide is thought to degrade rapidly. There is almost no difference in the reaction rate between the systems where hydrogen peroxide was added at the start of the leach compared to systems where no hydrogen peroxide was added after the initial 2 hours have passed.

2.3 Ion exchange

Ion exchangers are insoluble electrolytes that contain labile ions that can easily be displaced with ions from a surrounding medium without any physical change to the electrolyte's structure. This exchange of ions is reversible. The exchanging electrolyte is generally of a complex nature and a macromolecule. After dissociation all electrolytes exist in either their anionic or cationic form. As a result, the matrix carries a surplus charge. This surplus charge is neutralized by a labile counter ion of opposite charge. A cationic exchanger consists of macromolecule or anionic polymer with a negative charge and labile cations (A^+). The labile cations can be exchanged with mobile cations (B^+) in solution. The ion exchange mechanism can be expressed as in [2.13] and the opposite is true for an anionic exchanger as shown in [2.14] (Dorfner, 1991).

$$I^-A^+ + B^+ \leftrightarrow I^-B^+ + A^+ \qquad [2.13]$$

$$I^+Y^- + Z^- \leftrightarrow I^+Z^- + Y^- \qquad [2.14]$$

2.3.1 Classification of ion exchange resins

Synthetic ion exchange resins and their properties are a function of three decisive factors with regards to their production: the raw material used for the construction of the skeleton or matrix, the bridging agents used for cross-linking and insolubilization and their functional group. Ion exchange resins are furthermore classified as either weak or strong acidic resins or weak or strong basic resins (Dorfner, 1972). Basic resins act as Brønsted-Lowry bases and have labile anions that can act as proton acceptors. Acidic resins however act as Brønsted-Lowry acids and are proton donators. Basic anion resins will not be discussed in detail as the study focusses on metals in the cationic form.

Strong acidic cation resins typically have a sulfonic acid group like sodium polystyrene sulfonate and they tend to take up all cations. Their standard form is usually either H^+ or Na^+. They are sensitive for oxidative attacks which leads to the beads becoming soft and increased swelling in the beads. Iron and manganese pose problems with strong acid resins as they are not easily removed and tend to foul the resin thus reducing its lifetime. Strong acidic resins can be regenerated using a strong acid like sulphuric, hydrochloric or nitric acid. Weakly acidic cation resins typically have carboxylic acid groups. They tend to have higher chemical and mechanical stability, loading capacity and regeneration efficiency than strong acidic resins.

Chelating ion exchangers are resins that contain macromolecular polymeric materials that are covalently bonded and have reactive groups that can form inner complexes or chelates with selected ions. They tend to have higher selectivity for specific metal ions compared to conventional non-chelating resins. Ion exchange and complex formation takes place by both incorporating the metal ion into a ring and by chemical bonding after the metal replaces the labile ions of the resin.

$$I - H_2 + Me^{2+} \leftrightarrow I - Me + 2H^+ \qquad [2.15]$$

Equation [2.15] shows the reaction mechanism for the bonding of a metal with chelating ion exchanger. The exchanger acts as a Lewis base as it donated electrons and the metal acts as a Lewis acid (Edebali & Pehlivan, 2016).

Chelating ion exchange resins tend to have a slower exchange process compared to conventional ion exchangers. This seems to be the result of boundary layer diffusion, the second order chemical reaction, intraparticle diffusion or a combination of all the factors (Dorfner, 1991; Liebenberg, 2012; Zagorodni, 2007). Dorfner (1991) reports that the bonding strength in ordinary ion exchangers is in the order of 8 to 12kJ/mol while it is between 60 to

100kJ/mol for chelating ion exchangers. This increase in bond strength requires higher concentrations of eluting agent to successfully remove the metals from the ion exchanger.

There are a number of commercially available chelating ion exchange resins that are used for the recovery of metals that show a high affinity for copper. The functional groups or ligands of these resins include Bis-picolylamine (bis-PA), Iminodiacetic (IDA) and Aminophosphonic (AP) (Edebali & Pehlivan, 2016; Hamdaoui, 2009; Hubicki & Kołodyńska, 2012; Sengupta, 2017). For this study bis-PA and IDA resins were considered as they are the most commonly used resins for copper recovery in industry.

Both aforementioned chelating materials are commonly referred to as chelating ion exchangers, while bis-PA is in fact a chelating adsorbent. Figure 2.2 shows the functional groups of both IDA and bis-PA and how they chelate a metal. In IDA, a chelating ion exchanger, the metal cation acts as both the central atom and as counter ion for the negatively charged ligand. When looking at bis-PA, a chelating adsorbent, it can be seen that the neutral ligands form charged chelates with the metals and the anions are co-adsorbed (Sirola, 2009)

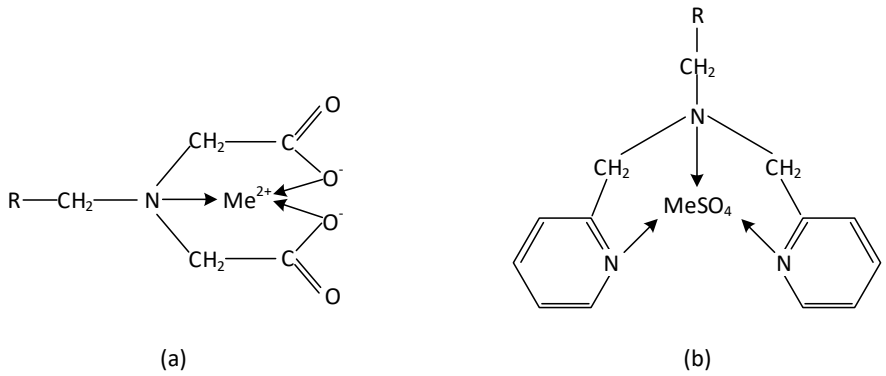

Figure 2.2: Chelating mechanism (a) IDA and (b) bis-PA resins

2.3.2 Selectivity of chelating materials

Interactions between the metals in a solution and the chelating materials depends on the properties of the solutions, metal and the ligand of the chelating material. The affinity between the metal and ligand has the most significant effect. These metal-ligand affinities can qualitatively be described using Pearson's hard and soft acids theory (Pearson, 1963) or more quantitatively using the ligand field theory (Cotton & Wilkinson, 1963; Sirola, 2009).

2.3.2.1 Pearson's Theory

According to Pearson (1963) one can explain the metal-ligand affinity with Lewis acid-base interactions. With a Lewis acid being an electron acceptor and a Lewis base an electron donor. Lewis acids and bases can be divided into six categories; hard, soft and borderline acids or bases. Hard acids and bases have small ionic radii, high oxidation states, low polarizabilities and high electronegativities. The opposite is true for soft acids and bases. Borderline acids and bases have intermediate hardness and no prediction can be made about the metal-ligand affinity. A hard acid will form a strong bond with a hard base and a soft acid will form a strong bond with a soft base (Liebenberg, 2012; Sirola, 2009).

Table 2.2: Lewis hard and soft acids and bases categorized (adapted from (Parr & Pearson, 1983; Sirola, 2009))

Acids			Bases		
Hard	**Soft**	**Borderline**	**Hard**	**Soft**	**Borderline**
$\mathbf{H^+}$	Cu^+	Mn^{2+}	OH^-	H^-	C_6H_7N
$\mathbf{Li^+}$	Ag^+	Fe^{2+}	RH^-	RS^-	C_5H_5N
$\mathbf{Na^+}$	Au^+	Co^{2+}	F^-	I^-	N_2
$\mathbf{K^+}$	Hg^+	Ni^{2+}	Cl^-	PR_3	N_3^-
$\mathbf{Mg^+}$	Cs^+	Cu^{2+}	NH_3	SCN^-	Br
$\mathbf{Ca^{2+}}$	Pd^{2+}	Zn^{2+}	CH_3COO^-	CO	NO_3^-
$\mathbf{Sn^{2+}}$	Cd^{2+}	Pb^{2+}	CO_3^{2-}	C_6H_6	SO_4^{2-}
$\mathbf{Al^{3+}}$	Pt^{2+}		N_2H_4		
$\mathbf{La^{3+}}$	Hg^{2+}				
$\mathbf{Cr^{3+}}$					
$\mathbf{Co^{3+}}$					
$\mathbf{Fe^{3+}}$					
$\mathbf{As^{3+}}$					

The ligands of IDA resins are carboxylic acids and thus hard bases, bis-PA resins have pyridine ligands and fall in the borderline base category. Copper and most other metals present on PCBs fall in the borderline category, they are also generally first line transition metal. No conclusion can thus be drawn on the metal-ligand affinity between these metals and IDA or bis-PA.

2.3.2.2 Ligand field theory

All first row transition metals have partially filled d-orbitals, this affects their complex formation and allows them to form high spin metal complexes. The Irving-Williams series describes the general stability of these metals and was found to be true for nearly all complexes irrespective of the nature of the ligand or amount of ligand molecules involved (Irving & Williams, 1953). The order of the series is $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, the

stability order is explained by the ligand field theory, this follows from considering the inverse of the atomic radii and the second ionization potentials of the metals (Irving & Williams, 1953). Changes in the natural bonding orbitals with changes in the ligand can lead to certain complexes with extremely high stabilities, as in the case of ferrous ions.

2.3.3 Kinetics of loading

The kinetics of copper loading on the resins can be determined by performing batch loading. Zainol & Nicol (2009) suggest that adsorption of metals onto the resin can be described by a three step process. Initially involving the mass transfer of the metal from the bulk solution to the surface of the resin followed by diffusion of the metal onto the resin bead (Fleming & Nicol, 1980; Zainol & Nicol, 2009). This process is shown in equation [2.16] with the subscripts s and r referring to the solution and resin respectively and superscript s referring to the surface of the resin.

Solution Surface Resin

$$[Me]_s \overset{k_s}{\rightarrow} [Me]_s^s \overset{K}{\rightarrow} [Me]_r^s \overset{k_r}{\rightarrow} [Me]_r \qquad [2.16]$$

k_s and k_r represent the mass transfer coefficients between the phases while K is the rate constant for the adsorption onto the resin. Faster adsorption kinetics are more desirable than higher loading capacities as higher flow rates can be accommodated, and the resin capacity is used to a further extent (Liebenberg, 2012).

First and second order models can be fitted to the approach to equilibrium data with equations as shown in [2.17] (Kołodyńska, Sofińska-Chmiel, Mendyk & Hubicki, 2014) for the first order model and [2.18] (Liebenberg, 2012) for the second order model.

$$\log(q_e - q_t) - \log(q_e) = -K \cdot t \qquad [2.17]$$

$$\frac{1}{q_e - q_t} - \frac{1}{q_e} = k \cdot t \qquad [2.18]$$

Where q_e refers to the equilibrium loading on the resin and q_t to the loading on the resin at time t. k can be found by plotting $-(\log(q_e - q_t) - \log(q_e))$ vs t for the first order model and $\frac{1}{q_e - q_t} - \frac{1}{q_e}$ vs t for the second order model. Fitting a straight line of best fit through the data will give k as the gradient.

2.3.4 Elution of metals

The elution of loaded resin is done to remove all the metals ions present on the resin. The eluent must be chosen so that the exchange ion of the eluent is the ion that is desired to be present on the resin for re-use, in industry it is common practise to perform the elution of resins using the spend acid solutions from cathodic production. Diluted acid mixtures are generally used for metals in the cationic form. The reaction taking place is the reverse of the reaction shown in equation [2.15]. The metallic cation of the resin is exchanged for hydrogen protons from the acidic solution. Reviewing of published work on the elution of copper from IDA and bis-PA resin has shown that eluting the resin with a 1 molar solution of sulphuric acid with a 1:5 ratio of resin to acid volume at a flow rate of 1 bedvolume per hour should successfully elute all the metals from the resin and return it to its hydrogen form (Yahorava, Kotze & Auerswald, 2014; Zhang, Cai, Wang, Bai, Zhou, Wu & Mao, 2010).

2.3.5 Effect of pH

Sirola (2009) describes that the pH affects ion exchange of metals as a result of competitive binding equilibrium between hydrogen protons and metal ions. The displacement of metal ions from the resin by hydrogen depends on the basicity of the ion exchanger. Dilute acids can displace metal ions from strongly basic ion exchangers, while the displacement of hydrogen by metals from the resin can be difficult and may pose problems as a result of metal precipitation.

The effect of pH on ion exchange is vastly different depending on the system involved. Veli & Pekey (2004) evaluated this effect on pH values ranging between 2 and 10. It was found that the extraction of copper with ion exchange was improved at lower pH values, as a result of $Cu(OH)_2$ formation at higher pH values and thus inhibiting the copper to be exchanged effectively, the optimum pH was found to be 4.5 with a copper concentration of 80mg/L, at this point almost all the copper was extracted. Das (2014) found similar results but with an optimum at a pH value of 7.45. A further increase of the pH resulted in low selectivities due to the high hydroxyl ion concentrations.

2.4 Solvent extraction

In solvent extraction an aqueous solution containing the metals of interest is contacted with an immiscible organic phase in a mixer-settler or column reactor. The metal ions in the aqueous phase react with the extractant in the organic phase during contact to form an organometallic complex. The two phases are subsequently allowed to separate causing the metal ions to be

extracted from the aqueous phase. Extractants are usually used in a dilute form to improve the extraction. Diluents need to be immiscible in water and improve physical properties such as the viscosity of the organic phase and create a greater difference in the density between the organic and aqueous phase allowing for better phase separation (Olivier, 2011).

The metals are recovered from the extractant by stripping with a strong acid, like nitric, sulphuric or hydrochloric acid. During this step the metal ions are replaced by hydrogen. This allows the solvent to be recycled and the metals ions are recovered for further processing like electrowinning, reduction or crystallization processes to recover solid products. Figure 2.3 shows a solvent extraction circuit as one would typically use for the recovery of copper from glycine leach liquors (Eksteen, Oraby & Tanda, 2017).

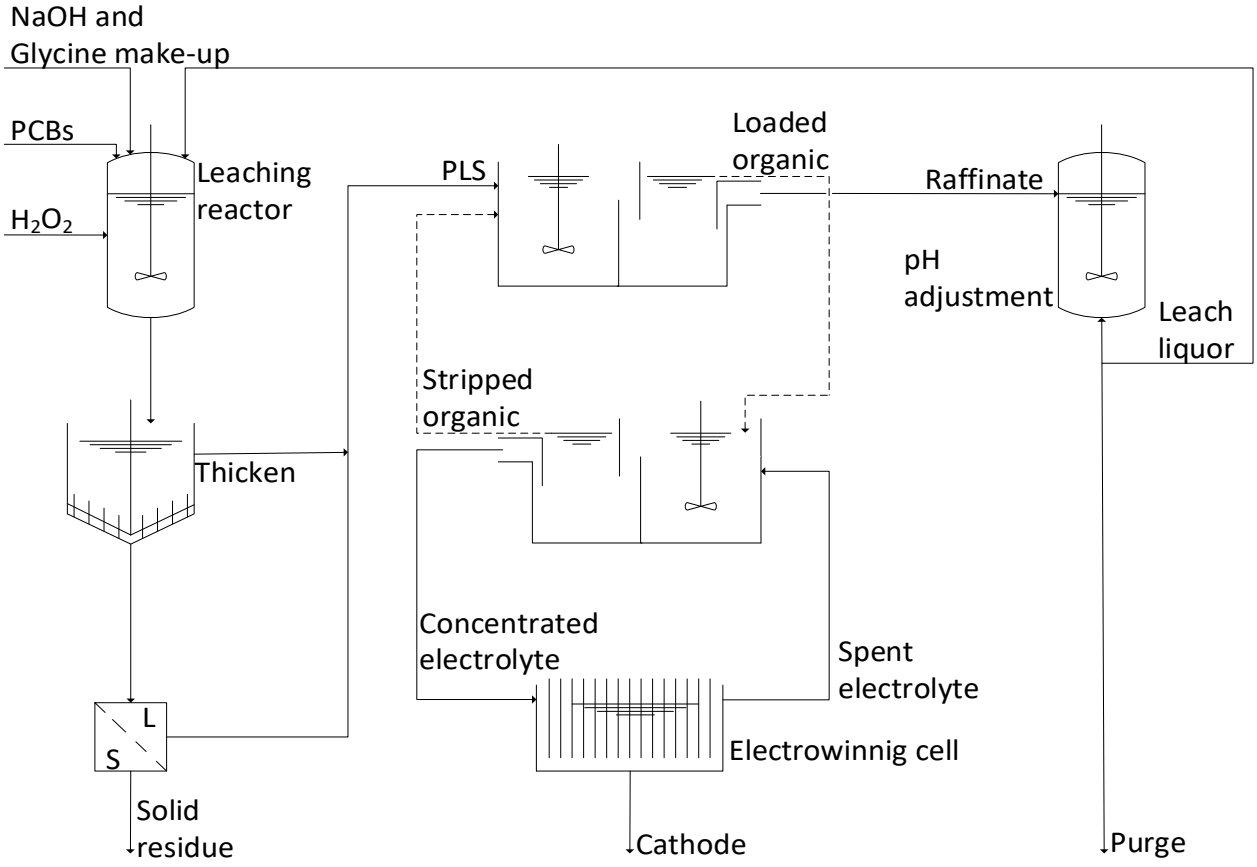

Figure 2.3: Schematic of solvent extraction circuit (adapted from (Eksteen *et al.*, 2017))

Solvent extraction is known to have lower operating and capital cost compared to alternatives like adsorption onto activated carbon or ion exchange (Eksteen *et al.*, 2017; Olivier, 2011; Tanda, Oraby & Eksteen, 2017).

2.4.1 Development of solvent extractants

Carboxylic and phosphoric acid were used in the 1950's to recover copper from magnesium but the co-extraction of iron(III) and thus the removal of iron from leach liquors by precipitation created a problem. This led to the development of oximes as extractants for copper (Pradhan & Mishra, 2015). $\beta-$ hydrooximes where initially used for the extraction of copper. Ketoxime reagents were later developed. The early ketoxime were produced using 2-hydroxybenzophenone while this was later replaced by 2-hydroxy-5-nonylacetophenone, like LIX-84I, which proved to be able to handle lower grade copper leach solutions, have better phase separation and low entrainment losses to the raffinate phase.

An extensive literature study was performed on available extractants and the effect of operating conditions on their performance. Table 2.3 highlights some of the literature that was considered in this thesis. From this literature it was decided to use LIX-84I for this research. It is very selective for copper under a wide range of operating conditions and has a high loading capacity. It has however not been studied to a significant extent on glycine leach solutions (Tanda, 2017).

Table 2.3: Selected research on solvent extractants.

Author	Extractant	Application
(Lazarova & Lazarova, 2005)	LIX-984N-I, LIX-84I, LIX-860N and LIX-65N	Comparative study on the extraction of copper from nitrate media. The effect of pH for values between -1 and 4.5 were investigated.
(Tanda, Oraby, *et al.*, 2017)	Mextral 84H and Mextral 54-100	Recovery of copper from alkaline glycine leach solutions. Effect of operating conditions such as pH, temperature and extractant concentration. Mextral 84H has the same functional group as LIX-84I, to be able to selectively recover copper from said leach liquors in wide range of conditions.
(Pradhan & Mishra, 2015)	Various	A review of current status of copper extraction with commercial solvents.
(Eksteen *et al.*, 2017)	LIX-84I	Conceptual process for the recovery of copper from chalcopyrite in alkaline glycine leach liquors. LIX-84I was tested as a possible

		solvent to extract copper form the said leach liquors. Proves highly selective with large distribution factors.
(Ali, Daoud & Aly, 1996)	LIX-84I	Recovery of copper from sulphate medium with LIX-84I in kerosene. Effect of pH, metal concentration, extractant and strip solution concentration as well as loading capacity were investigated.
(Hu & Wiencek, 2000)	LIX-84	Modelling of equilibrium data using concentration based model together with activity based models.
(Kyuchoukov, Bogacki & Szymanowski, 1998)	LIX-84 and LIX-54	Copper extraction from ammoniacal solutions, using a mixture of LIX-84 and LIX-54. Li-54 acts as modifier for LIX-84 enhancing extraction.
(Panigrahi, Parhi, Sarangi & Nathsarma, 2009)	LIX-84I and LIX-662N	Extraction of copper from sulphide leach liquor using LIX-84I and LIX-622N diluted with kerosene.
(Rodríguez, Aguilar, Bernal, Ballinas, Rodríguez, de Gyves & Chimmel, 1997)	LIX-984	Extraction of Cu(II), Fe(III), Ga(III), Ni(II), In(III), Co(II), Zn(II) and Pb(II) from salt solutions. Effect of pH was investigated and reported on.

2.4.2 Extraction process and equilibrium data

Extraction of copper can be described as in equation [2.19] for a general case and more specifically for copper from a glycine leach liquor as in equations [2.20]. Stripping using a strong acid can be written as in [2.21].

$$2RH_{(org)} + Cu^{2+}_{(aq)} \leftrightarrow R_2Cu_{(org)} + 2H^+ \quad [2.19]$$

$$2RH_{(org)} + Cu(H_2NCH_2COO)_{2\,(aq)} \leftrightarrow R_2Cu_{(org)} + 2H_2NCH_2COOH_{(aq)} \quad [2.20]$$

$$R_2Cu_{(org)} + 2H^+_{(aq)} \leftrightarrow 2RH_{(org)} + Cu^{2+}_{(aq)} \quad [2.21]$$

It is necessary to introduce a distribution coefficient, separation factor and percentage extraction to understand and quantify the performance of extractants, these variables can be represented as shown in equations [2.22], [2.23] and [2.24].

$$D_A = \overline{C_A}/C_A \quad [2.22]$$

$$\alpha_B^A = \frac{D_A}{D_B} \quad [2.23]$$

$$\%E_A = \frac{C_{A0} - C_A}{C_{A0}} \quad [2.24]$$

Where D_A represents the distribution factor of A, $\overline{C_A}$ the concentration of A in the organic phase, C_A the concentration of A in the raffinate, α_B^A the separation factor of A over B, $\%E_A$ the percentage extraction of A and C_{A0} the feed concentration of A.

A higher distribution coefficient indicates higher extractability of a metal using the specific solvent, while a large separation factor indicates that a solvent can selectively extract A over B.

2.4.3 Representation of equilibrium data

Extraction isotherms are commonly used in solvent extraction to represent equilibrium data, this can be used to determine the number of equilibrium stage needed to extract a metal from the aqueous phase.

On an isotherm the concentration of the metal in the organic phase is shown on the y-axis and the concentration in the aqueous phase on the x-axis. By adding an operating line with the gradient of the ratio of aqueous to organic (A:O) stages can be stepped off. Figure 2.4 shows a

hypothetical isotherm and it shows the construction to determine the amount of stages needed to remove 90% of metal, M, from the aqueous phase with an A:O of 2:1 (Kislik, 2012).

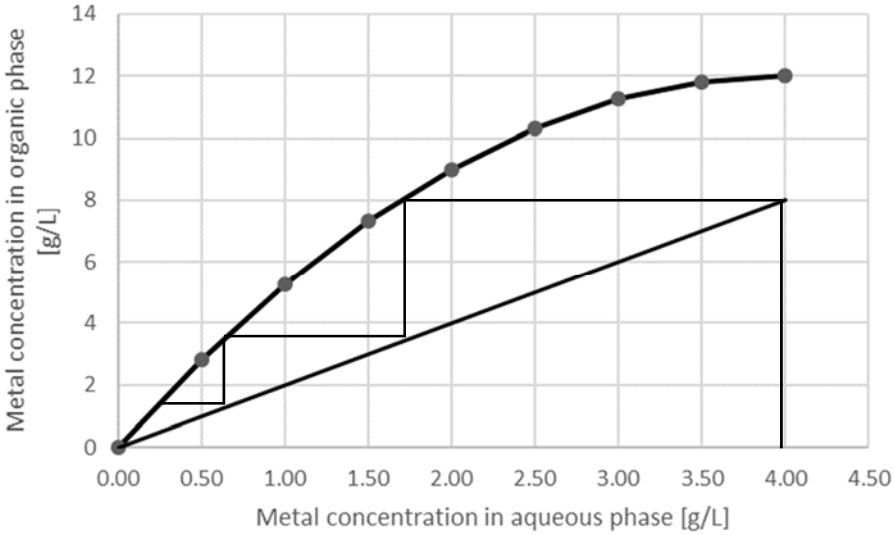

Figure 2.4: Hypothetical extraction isotherm with stages stepped of

2.4.4 Effect of pH

From equation [2.20] one can see that hydrogen atoms are released during the extraction of copper from the leach solutions, this suggest that an increasing pH should increase the extraction of copper since this allows the aqueous phase to return to its natural acidity. Tanda (2017) reported a slight increase in the extraction of copper from a glycine leach liquor, the extraction went from 99.49% at a pH of 9 to 99.68% at a pH of 12. The minimal difference in extraction is because almost complete extraction already occurred at the lower pH values as the initial leach solution contained only 2g/L of copper. Eksteen, Oraby & Tanda (2017) reported a more significant increase from 98.8% to 99.4% when increasing the pH from 8.8 to 10, with an initial copper concentration of 3.6g/L

2.4.5 Stripping of solvent

Stripping of a solvent occurs as shown in equation [2.21], the stripping agent needs to be mutually insoluble with the solvent to prevent fouling of the solvent. It must also be able to successfully extract the solute from the solvent phase. In the copper industry sulphuric or nitric acid are widely used to strip copper from solvents (Kislik, 2012). Stripping can be used to further concentrate the final copper solution that can then be send for electrowinning or other solid product recovery methods.

The equilibrium between the solvent and the stripping agent can be modelled as a new solvent extraction system where the solvent now becomes the carrier and the stripping agent the solvent. This equilibrium data can also be represented on an extraction isotherm as discussed in section 2.4.3 to predict the number of stripping stages needed for complete stripping.

3 EXPERIMENTAL METHOD

This section covers the experimental method, experimental design and all materials used. The preparation of the synthetic pregnant leach solution is discussed in section 3.1. Section 3.2 covers the ion exchange tests performed and section 3.3 the solvent extraction tests. The analytical methods that were used are discussed in section 3.4.

3.1 Synthetic pregnant leach liquor

A synthetic pregnant leach solution (PLS) was prepared to perform all experimental work that was needed to reach the objectives of this study as stated in section 1.2. A PLS was prepared in batches using leaching conditions as suggested in literature and the metals were added as metallic powders in the same proportions as found on PCBs to reduce the variability introduced by using PCBs.

3.1.1 Conditions and materials

The amount of metals powder added was based on the concentrations found in literature as shown in table 2.1. Table 3.1 shows the amount of metals representative of 100g of PCBs and Table 3.2 the leaching conditions used for the preparation of the PLS. Table 3.3 shows the chemicals that were and their purities.

Table 3.1: Mass of metals representative of 100g of PCBs

Metal	mass [g]
Cu	20
Al	4
Pb	2
Zn	1
Ni	1
Fe	4
Sn	3

Table 3.2: leaching conditions for synthetic pregnant leach solution

Initial pH	Glycine concentration [M]	Hydrogen peroxide (32%) [mL/hour]	Temperature	Solid to liquid ratio	Residence time [h]
8	1.5	15	Ambient	1:10	72
10	1.5	15	Ambient	1:10	72
11	1.5	15	Ambient	1:10	72

Table 3.3: Chemicals used for PLS preparation

Substance name	Substance formula	Concentration/purity [weight%]	Concentration/purity [M]	Molar mass [g/mol]
Glycine	$C_2H_5NO_2$	99%	-	75.07
Sodium hydroxide	NaOH	50%	18.94	40
Hydrogen peroxide	H_2O_2	30%	9.7	34
Copper	Cu	99%	-	63.55
Aluminium	Al	99%	-	26.98
Lead	Pb	99%	-	207.2
Zinc	Zn	99%	-	65.41
Nickel	Ni	99%	-	58.69
Iron	Fe	99%	-	55.85
Tin	Sn	99%	-	118.71

3.1.2 Equipment

The synthetic PLS was produced in a 5L beaker with an overhead agitator motor, a Teflon 4 blade stirrer, and a pre-calibrated peristaltic pump to continuously feed hydrogen peroxide. The stirrer was placed around 20mm above the bottom of the vessel and continuously agitated the mixture at 600RPM. pH measurements were done using a Eutech pH6+ palmtop pH meter. All samples were taken in 15mL centrifugal tubes using 10mL syringes and 0.22micron syringe filters. The solid residue was separated from the PLS using a filter paper in a Buchner flask and funnel connected to a vacuum pump.

3.1.3 Procedure

In order to produce the PLS, glycine and the metal powders were weighed off and the glycine was added to the 5L beaker. 1.8L of de-ionized water was added to the beaker and stirring turned on at a low speed (200rpm) allowing the glycine to completely dissolve. pH measurements were taken, and sodium hydroxide was added to adjust the pH to the desired value. The solution of desired pH was poured into a volumetric flask, topped to 2L and poured back into the 5L beaker. A final pH measurement and adjustment was done. The pipe of the peristaltic pump was secured just above the liquid level in the beaker and the metal powders slowly added after stirring and the peristaltic pump were turned on.

Samples were taken at 0, 1, 2, 4, 8, 12, 24, 48 and 72 hours after the start and diluted with a 2% nitric acid solution. After 72 hours the samples were analysed for copper content on an atomic absorption spectrometer to confirm that equilibrium was reached.

The overhead stirring was stopped, and the solution filtered using a filter on a Buchner funnel and flask connected to a vacuum pump. A sample was taken from the liquid to be analysed using ICP-AES and the rest was stored in a marked and sealed glass flask for later use, the solid residue was discarded of in a safe manner.

3.1.4 Composition of pregnant leach solution

Table 3.4 shows the range metal concentrations that was found in the PLS as measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES).

Table 3.4: Average metal content of PLS

Metal	Al	Cu	Fe	Ni	Pb	Sn	Zn
Concentration [g/L]	0.2-0.4	9-12	0.02	0.00	1-1.5	0.00	0.9-1.2

3.2 Ion exchange

Testing of ion exchange resins was performed using stirred beaker tests to investigate the equilibrium conditions of the resins. This was followed by column elution tests on selected resins. The following resins were investigated:

- Purolite S930Plus, a high capacity macroporous iminodiacetic acid chelating resin produced by Purolite. It has a polystyrene crosslinked with divinylbenzene polymer structure and shipped in the Na^+ form.
- Lewatit MonoPlus TP207, a macroporous iminodiacetic acid chelating resin on a crosslinked polystyrene matrix produced by Lanxess, also shipped in the Na^+ form.
- Lewatit MonoPlus TP220, a microporous bis-picolylamine chelating resin on a crosslinked polystyrene matrix produced by Lanxess.

No in-depth optimization was done on ion-exchange as it proved not to be effective to selectively recover copper from the PLS. This will be discussed in detail in section 4.1.

3.2.1 Stirred beaker test

3.2.1.1 Design of experiments

Resin to liquid ratios of 1:5, 1:25 and 1:50 were tested for the screening tests. Table 3.5 shows the conditions used for the various experimental runs.

Table 3.5: Ion exchange equilibrium loading tests

Run no.	Resin	R:L ratio	PLS volume [mL]	Resin volume [mL]
1	S930Plus	1:5	250	50
2	S930Plus	1:25	250	10
3	S930Plus	1:50	250	5
4	TP220	1:5	250	50
5	TP220	1:25	250	10
6	TP220	1:50	250	5
7	TP207	1:5	250	50
8	TP207	1:25	250	10
9	TP207	1:50	250	5

The PLS used was as discussed in the previous section and the resins were used in their H^+ form. The method for converting the resins to the H^+ form is discussed in section 3.2.2.

3.2.1.2 Experimental setup

The experimental setup was as shown in figure 3.1, consisting of a 500mL beaker with an overhead stirrer and continuous pH control with an on/off type controller. Sodium hydroxide was used for the pH correction.

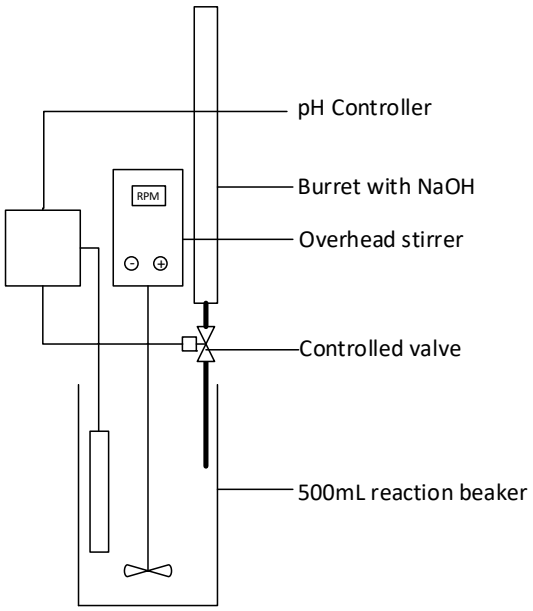

Figure 3.1: Experimental setup for pre-screening and saturation isotherm tests

3.2.1.3 Experimental procedure

The PLS was poured into a beaker and a liquid sample was taken as the initial feed sample, the correct volume was then measured using a volumetric flask. Measuring the correct volume of resin was done in a measuring cylinder filled with water. A small amount of resin was added and allowed to settle, additional resin was added or removed until the correct amount was measured off. De-ionized water was used to rinse all the resin out of the measuring cylinder into the beaker. A pipette was used to remove the excess water from the resin and the PLS was added to the beaker. Stirring and pH control were turned on. The stirring was switched off to allow the resin to settle when liquid samples were taken.

Liquid samples were taken at 0, 0.5, 1,2,4,8,12 and 24 hours after the start of the run. The resin was filtered from the PLS and stored in a sealed container for use in the column elution tests as discussed in the following section.

3.2.2 Elution and conversion of resins

Acidic ion exchange resins are commonly shipped with their labile ion being Na^+, while H^+ labile ions were needed for this research. The resins were converted to H^+using 5 bedvolumes of 3M sulphuric acid. Elution tests were performed for both S930Plus and TP207, using the resin from the 1:5 ratio stirred beaker. The elution was performed using 1.5M sulphuric acid at a flowrate of 2 bedvolumes per hour.

The setup and procedure that was used to perform the elution tests and to convert the resin from the Na^+ form to H^+ was the same. This method will be discussed in the following section.

3.2.2.1 Experimental setup

The setup used for column test was as shown in figure 3.2. Consisting of three beakers, two peristaltic pumps, a glass column with filters fitted on both sides and four valves, two at the top and bottom. One of the valves at the top is used to stop the flow from the peristaltic pump and the other to vent the column. One of the bottom valves was for sampling and the other valve to connect the peristaltic pump for backwashing the column.

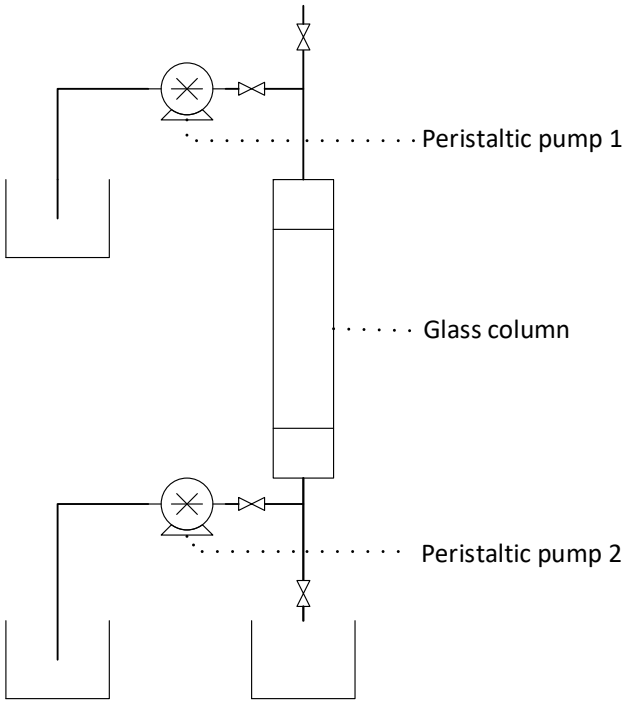

Figure 3.2: Experimental setup for column tests

3.2.2.2 Experimental procedure

The resin was measured off in a measuring cylinder in the same manner as for the equilibrium loading tests and transferred to the column. The column was subsequently backwashed for 15-20 minutes by pumping de-ionized water through the column from the bottom up using pump 2. After allowing the resin to settle, the excess water above the resin was allowed to drain through the bottom valve. The freeboard area above the resin was carefully filled with the process fluid while ensuring that the resin bed was not disturbed. Peristaltic pump 1 was turned on at the desired flowrate with both the bottom valves closed and the top vent open to ensure that the pipes are filled with process fluid. To start the elution, the sample valve at the bottom was open while at the same moment closing the vent valve. The eluate was collected in 50mL sample tubes for the elution tests. The effluent from the conversion steps was drained into a waste container.

3.3 Solvent extraction

Solvent extraction tests were done using LIX-84I extractant that was obtained from BASF. The extractant was used as is and diluted using kerosene. The effect of pH and extractant concentration on the extraction selectivity for copper was evaluated. The effect of acid

concentration and aqueous to organic ratio (A:O) on stripping was also evaluated. This data was used to create equilibrium isotherms and suggest a flowsheet for the recovery of copper from glycine leach liquors.

3.3.1 Design of experiments

A full factorial experimental procedure was performed for single stage extraction from leach liquors while varying the extractant concentration, pH of PLS and the aqueous to organic ratio. Table 3.6 shows the experimental design, 3 variables at 3 conditions were tested, resulting in 27 experiments, half of them were repeated for repeatability tests. The parameters are as shown in table 3.7.

Table 3.6: Solvent extraction experimental design

	A	B	C
1	-1	-1	-1
2	-1	-1	0
3	-1	-1	1
4	-1	0	-1
5	-1	0	0
6	-1	0	1
7	-1	1	-1
8	-1	1	0
9	-1	1	1
10	0	-1	-1
11	0	-1	0
12	0	-1	1
13	0	0	-1
14	0	0	0
15	0	0	1
16	0	1	-1
17	0	1	0
18	0	1	1
19	1	-1	-1
20	1	-1	0
21	1	-1	1
22	1	0	-1
23	1	0	0
24	1	0	1
25	1	1	-1
26	1	1	0
27	1	1	1

Table 3.7: Solvent extraction tests parameters

Parameter	**A** Extractant concentration	**B** pH	**C** A:O ratio
-1	5%	8	1:1
0	10%	10	1:2
1	20%	11	1:4

Three stage extraction tests were also performed, the same PLS was contacted with fresh extractant in three consecutive stages. Three levels of extractant concentration and A:O were tested. Table 3.8 shows the experimental design for the three stage extractions tests and table 3.9 parameters for these tests.

Table 3.8: 3 stage solvent extraction experimental design

	A	**B**
1	-1	-1
2	-1	0
3	-1	1
4	0	-1
5	0	0
6	0	1
7	1	-1
8	1	0
9	1	1

Table 3.9: 3 stage solvent extraction tests parameters

Parameter	**A** Extractant concentration	**B** Aqueous:Organic ratio
-1	5%	1:1
0	10%	1:2
1	20%	1:4

Stripping performance was evaluated using by varying the concentration of the sulphuric acid and the acid to organic ratio.

Table 3.10 shows the experimental design for the stripping tests and Table 3.11 the test parameters for these tests. To ensure a uniform feed for the stripping experiments, a large batch of 20% LIX-84I was contacted with pH 10 PLS and a 1:1 A:O ratio.

Table 3.10: Stripping tests experimental design

	A	B
1	-1	-1
2	-1	0
3	-1	1
4	0	-1
5	0	0
6	0	1
7	1	-1
8	1	0
9	1	1
10	2	-1
11	2	0
12	2	1

Table 3.11: Stripping tests parameters

Parameter	A	B
	Sulphuric acid concentration	A:O ratio
-1	0.5M	1:1
0	1M	1:2
1	2M	1:4
2	3M	-

3.3.2 Experimental setup and procedure

The experimental setup consisted of a 500mL beaker on magnetic stirrer hotplate. The separation of the phases was achieved using a separation funnel.

The first step of the equilibrium tests was to measure the correct amount of extractant and to add kerosene as the diluent to obtain the solvent. This was placed in the 500mL beaker and the magnetic stirrer was turned on. The PLS was measured in a measuring cylinder and a liquid sample was taken before adding the correct amount to the solvent. After 10 minutes stirring was stopped, and the phases were allowed to separate. The aqueous and organic phases were separated using a separation funnel. A final sample was taken from the raffinate phase before discarding it.

The organic phase was stripped with 3M sulphuric acid in a 1:1 ratio except for the stripping optimization tests. The procedure for the stripping was the same as described for the equilibrium tests.

3.4 Analytical

All the analysis were done using either an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) or Flame Atomic Absorption spectrometer (AAS).

The repeatability of the AAS was confirmed by diluting the same sample three times at different dilutions and analysing each sample three times. The results are shown in Table 3.12.

Table 3.12: Repeatability of AAS

Dilution	concentration [g/L]	Average [g/L]
401	12.61	
401	12.36	12.52
401	12.60	
590	12.96	
590	12.84	12.88
590	12.85	
1001	12.23	
1001	12.02	12.12
1001	12.11	
	Overall average	12.51

The actual concentration was 12.5 g/L, the standard deviation was 0.3g/L.

4 RESULTS AND DISCUSSION

The results of the experimental work performed for this research is discussed in this chapter. Section 4.1 focussed on ion exchange with section 4.1.1 discussing the selectivity of the ion exchange resins for copper. Section 4.1.2 the loading kinetics of the resins and 4.1.3 the column elution results. Section 4.1.4 gives a conclusion on the viability of ion exchange for the intended process. Section 4.2 discusses the solvent extraction results. In 4.2.1 the selectivity of the extractant for copper is discussed and the effect of pH and extractant concentration are discussed in sections 4.2.2 and 4.2.3 respectively. Sections 4.2.4 and 4.2.5 discuss the equilibrium isotherms and the stripping of copper from the extractant. In 4.2.7 a conclusion on the use of solvent extraction for the recovery of copper from glycine leach liquors is drawn.

Mass balance reconciliation was done on all the experimental results and the results are shown in appendix B together with the repeatability tests.

4.1 Ion exchange

4.1.1 Selectivity for copper

The resins as discussed in 3.2.1 were used to test for their ability to selectively remove copper from the PLS with the procedure as in section 3.2.1.3. The results from these tests are shown in figures 4.1 and 4.2, it should be noted that only the results for aluminium, copper, lead and zinc are reported as the other metals did not leach to a significant extent.

All the resins showed a higher copper concentration on the resin compared to the other metals. However, when looking at the percentage extraction, lead and zinc showed almost 100 % extraction for both IDA resins while copper only had a 45% and 35% for S930Plus and TP207 respectively. S930Plus removed no measurable aluminium, but TP207 did remove almost 10%. The aluminium concentration on the resin was 0.17g/L. Lin & Juang (2005) investigated the effect of pH on the selectivity of Amerberlite IRC 748, an IDA resin, for copper in a copper-zinc leach liquor. They reported that almost no zinc was adsorbed at pH values below 2. But no differentiation in the adsorption of copper and zinc could be made at pH value above 4. A similar sharp increase in the adsorption of lead at pH values higher than 3 was reported by Wang, Chen & Chang (2002). This decrease in the selectivity for copper could be explained by looking at equation [2.15], from which it is clear that an increasing pH will push the reaction to the right. This will increase the loading capacity for all metals, thus reducing selectivity.

TP220, a bis-PA resin, only removed 7%, 13%, 8% and 9.5% of aluminium, copper, lead and zinc respectively, the highest concentration on the resin was copper with 6g/L, all the other metals had concentrations of less than 1g/L.

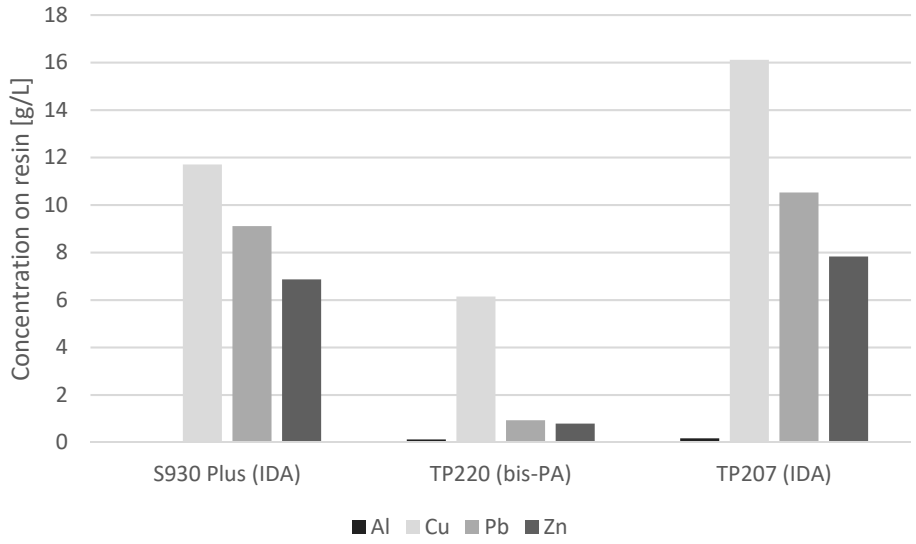

Figure 4.1: Equilibrium concentration on resins at 1:5 liquid to resin ratio

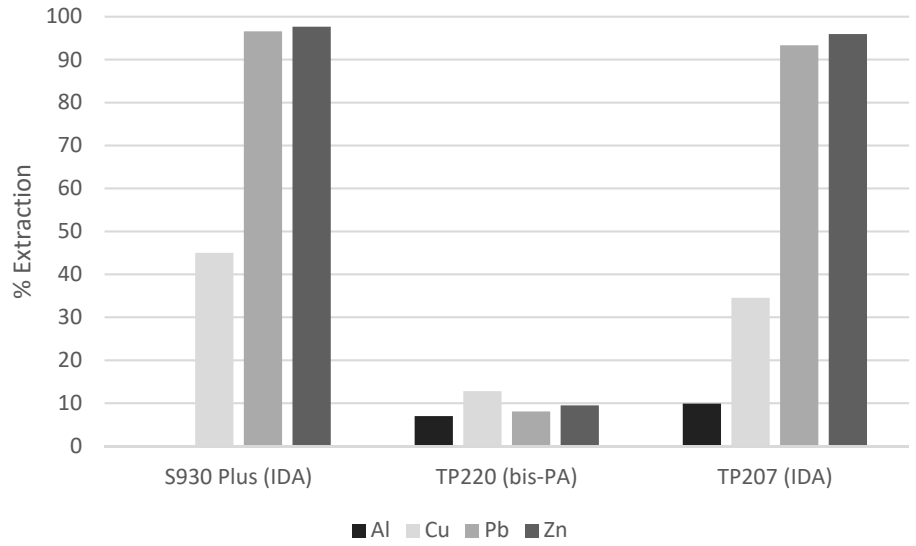

Figure 4.2: Percentage extraction at 1:5 liquid to resin ratio

The selectivities and separation factors of copper over aluminium, lead and zin are shown in table 4.1 for the resins tested. These values were calculated using equations [2.22] and [2.23].

Table 4.1: Separation factors for copper with regards to aluminium, lead and zinc

Resin type	α_{Al}^{Cu}	α_{Pb}^{Cu}	α_{Zn}^{Cu}
S930Plus	-	0.03	0.02
TP220	1.96	1.67	1.40
TP207	4.81	0.04	0.02

Both IDA resins have higher affinities for lead and zinc than copper, as evident from the low (<< 1) selectivity of copper relative to these metals. TP207 showed an almost 5 times higher affinity for copper than aluminium, while S930Plus adsorbed no aluminium and the separation factor would thus be infinite.

TP220 showed a slightly higher affinity for copper over aluminium, lead and zinc. This is in contradiction with the findings of Hubicki & Kolodyńska (2012) who reported minimal change in the selectivity of Dowex M4195, a bis-PA resin, in the pH range from 4 to 10.

The low selectivities for copper from all the resins tested indicated that the ion exchange resins are not capable of selectively adsorbing copper from the alkaline glycine leach liquor.

The differences between S930Plus and TP207 which are both IDA resins can be because of variations in the synthesis procedure. This causes differences in the structure of the matrix, degree of cross linking, density of functional groups and the particle size. The degree of cross linking has an effect on the moisture content of the resin which has an effect on the loading kinetics and selectivity of a resin (Hubicki & Kołodyńska, 2012; Liebenberg, 2012; Zainol & Nicol, 2009). The datasheet of S930 Plus indicates that the resin moisture retention of up to 60% and shows a reversible swelling of 35% from the H^+ to the Na^+ form. TP207 has a water retention of 58% and reversible swelling of 30%. A high moisture content indicates that the resin pores are larger, and the functional groups spaced further apart. This will also negatively influence the kinetics of loading.

4.1.2 Kinetics of loading

The kinetics of loading were modelled with the methods as discussed in section 4.1.2. Plots of the approach to equilibrium data for copper adsorption onto the resins are shown in figure 4.3.

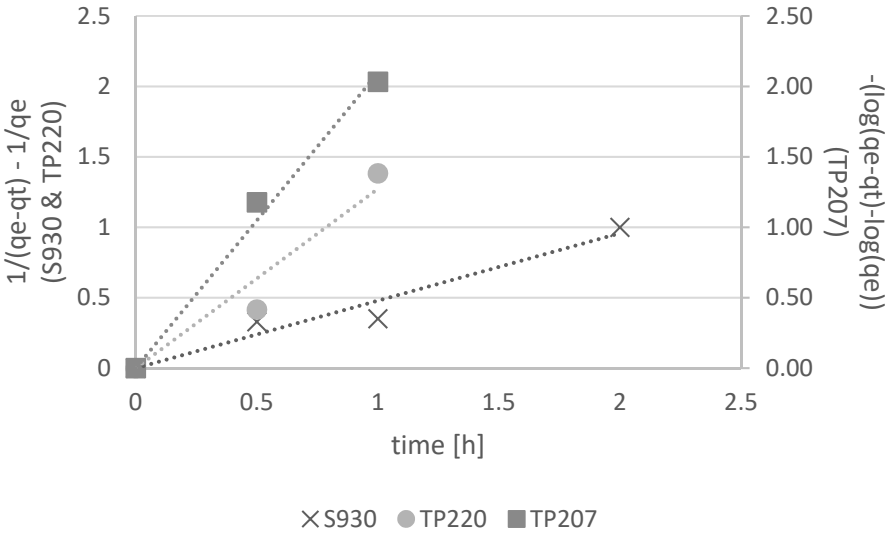

Figure 4.3: Kinetic data for copper adsorption

It was found that S930Plus and TP220 had the best fit with the second order model and TP207 with the first order model. A second order model indicates that the ion-exchange reaction is the limiting steps as the rate of mass transfer from the bulk solution to the resin surface is first order. S930Plus had the slowest kinetics, only reaching equilibrium after 2 hours, while both TP220 and TP207 reached equilibrium after 1 hour. The rate constants for the resins are shown in table 4.2 together with the R^2 value for the line of best fit.

Table 4.2: Kinetic constants for resins

Resin type	k	R^2
S930	0.479	0.95
TP220	1.272	0.94
TP207	2.097	0.99

4.1.3 Column elution

Column elution tests were performed as discussed in section 3.2.2. S930Plus and TP207 were investigated in these tests as they showed significantly higher equilibrium concentrations of copper compared to TP220. Figure 4.4 and 4.5 show the concentration against the amount of bedvolumes of acid for copper, lead and zinc from the elution test for S930Plus and TP207.

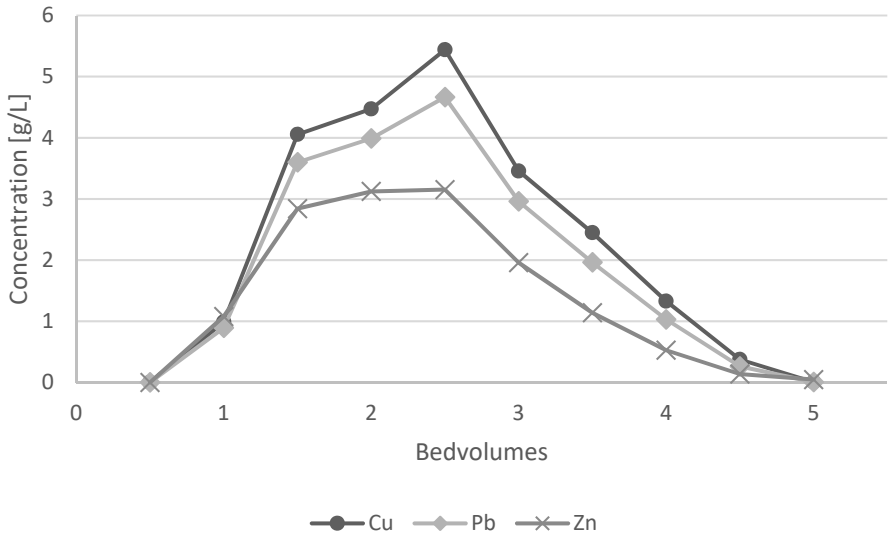

Figure 4.4: Elution of S930Plus using 1.5M H_2SO_4

All the metals were successfully eluted from S930Plus using 1.5M of sulphuric acid after 5 bedvolumes. With TP207 all the metals were eluted after only 4 bedvolumes. This resulted in a maximum concentration of 5.5g/L coper, 4.7g/L lead and 3.2g/L zinc from S930Plus and 8g/L copper, 6.2/L lead and 5.2g/L zinc from TP207.

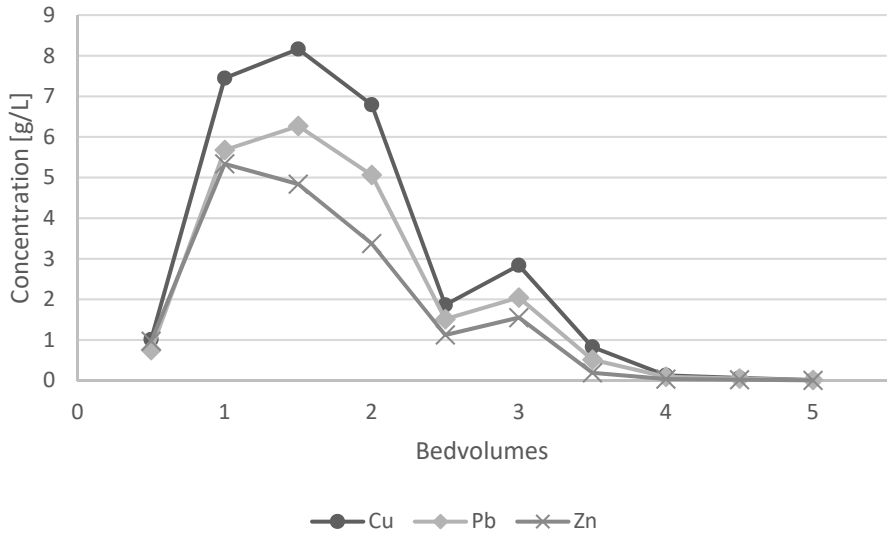

Figure 4.5: Elution of TP207 using 1.5M H_2SO_4

All the metals showed similar elution kinetics, indicating that split stripping would not be possible from the resins investigated. A difference in the elution behaviour of the metals is needed for split elution to be possible.

4.1.4 Conclusion

The recovery of copper from alkaline glycine leach liquors was proven to be ineffective using commercially available ion exchangers. Both iminodiacetic acid resins tested, S930Plus and TP207, showed no selectivity of copper over lead or zinc at the conditions that were tested. The separation factors found were 0.03 and 0.02 for copper over lead and zinc respectively with S930Plus, for TP207 the values were 0.04 and 0.02 for copper over lead and zinc respectively. S930Plus had equilibrium resin concentration of 11.7g/L copper, 9.1g/L lead and 6.7g/L zinc, and TP207 showed equilibrium concentrations of 16.1g/L copper, 10.5g/L lead and 7.8g/L zinc. Column elution tests showed that all the metals are removed at a similar rate indicating that split elution would also not be an option for the purification of copper. The concentrations found in the eluate were 5.5g/L coper, 4.7g/L lead and 3.2g/L zinc from S930Plus and 8g/L copper, 6.2/L lead and 5.2g/L zinc from TP207. The bis-picolylamine resins tested, TP220, showed separation factors of 1.67 and 1.40 for copper over lead and zinc respectively, these values are relatively close to 1 and effective separation of the metals was not achieved, the equilibrium concentrations were, 6.1g/L for copper, 0.9g/L lead and 0.8g/L zinc.

4.2 Solvent extraction

Experimental work was performed to investigate and quantify the ability of solvent extraction to successfully recover copper from glycine leach liquors. The selectivity for copper will be discussed in section 4.2.1 and the effect of pH in 4.2.2. The isotherms are discussed in section 4.2.4 and section 4.2.5 discusses the optimization of the stripping stage.

4.2.1 Selectivity for copper

The selectivity LIX-84I for copper was evaluated in preliminary tests using varying pH values from 8 to 11 and LIX-84I concentrations from v/v5% to v/v20%. At none of the operating conditions tested was any other metal extraction observed besides copper. The concentrations of the other metals in the PLS did not change from the feed sample before contact with the solvent to the raffinate sample after extraction. This was also confirmed by the fact that no other metals could be measured in the stripping liquor.

4.2.2 Effect of pH

The effect of pH on the recovery of copper from a glycine leach liquor was investigated by adjusting the pH of the PLS with sodium hydroxide or sulphuric acid. 10% and 20% solutions of LIX-84I diluted with kerosene were used as the extractants in a single extraction stage with an A:O ratio of 1:1, glycine concentration of 1.5M. Table 4.3 shows the initial aqueous copper concentration (C_{Cu0}), equilibrium aqueous copper concentration (C_{Cu}), equilibrium concentration in the organic phase ($\overline{C_{Cu}}$) together with the % extraction.

Table 4.3: Effect of pH on extraction using LIX-84I

LIX-84I concentration	pH	C_{Cu0} [g/L]	C_{Cu} [g/L]	$\overline{C_{Cu}}$ [g/L]	$\%E_{Cu}$
10%	8	2.2	1.2	0.81	47%
	10	10.2	6.2	4.1	39%
	11	10.3	4.1	6.2	60%
20%	8	2.2	0.6	1.5	74%
	10	10.5	3.7	5.7	64%
	11	10.1	1.4	8.7	86%

It is clear from the table above that increasing the pH of the PLS from 10 to 11 increases the extraction. A 21% and 22% increase can be seen at LIX-84I concentrations of 10% and 20% respectively. This as expected when looking at equation [2.19]. The system will compensate for the higher pH by shifting to the right as there is a deficiency of hydrogen atoms. The system will thus try to compensate for this.

Lowering the pH of the PLS reduced the solubility of copper as a result of the change in the dominant species of glycine as shown in equation [2.1] and figure 2.1. The initial copper concentration in the PLS was 2.2g/L at a pH 8 compared to 10g/L at pH 10 and 11.

4.2.3 Effect of extractant concentration

The effect of the extractant concentration was studied by performing a single stage extraction while keeping the pH of the PLS constant at 10, A:O ratio at 1:1 and the glycine concentration at 1.5M. The concentration of LIX-84I diluted with kerosene was varied between 20 and 5%.

Table 4.4 shows the data obtained from the experiment, with the variables as in table 4.3. A sharp increase in the extraction of copper was seen as the concentration of LIX-84I was increased. This is again a result of the equilibrium of the reactions as in equations [2.19] and [2.20], as an increasing extractant concentration will push the equilibrium to the right.

Table 4.4: Effect of LIX-84I concentration on extraction

LIX-84I concentration	C_{Cu0} [g/L]	C_{Cu} [g/L]	$\overline{C_{Cu}}$ [g/L]	$\%E_{Cu}$
5%	10.0	8.3	1.8	17%
10%	10.2	6.2	4.1	39%
20%	10.5	3.7	5.7	64%

Figure 4.6 shows the data from table 4.4 graphically. The graph shows that the extraction follows an almost linear increase with an increasing extractant concentration.

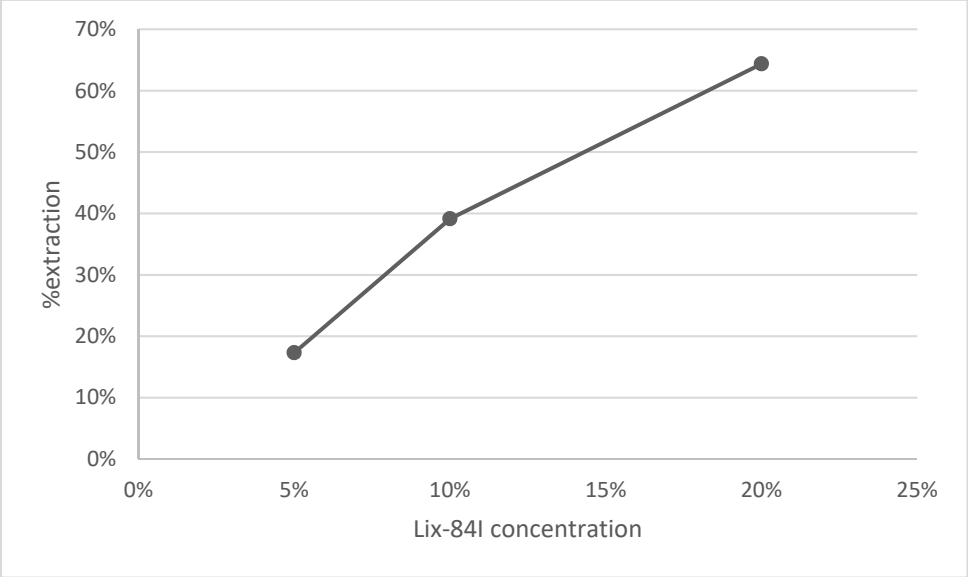

Figure 4.6: Effect of LIX-84I concentration on extraction

4.2.4 Isotherms

Extraction isotherms as discussed in section 2.4.3 were constructed using experimental data. A 3-stage extraction was performed with three concentrations of LIX-84I at various A:O ratios on a PLS with pH 10 and a glycine concentration of 1.5M. After each extraction stage a small sample of the aqueous phase was taken for analysis. The organic phase was stripped with 3M sulphuric acid in a 1:1 ratio as this proved to strip 100% of the copper from the organic phase (discussed in section 4.2.5). The PLS was contacted with extractant 2 more times. The results from these tests are shown in figure 4.7 with equilibrium isotherm drawn in using graphical estimation.

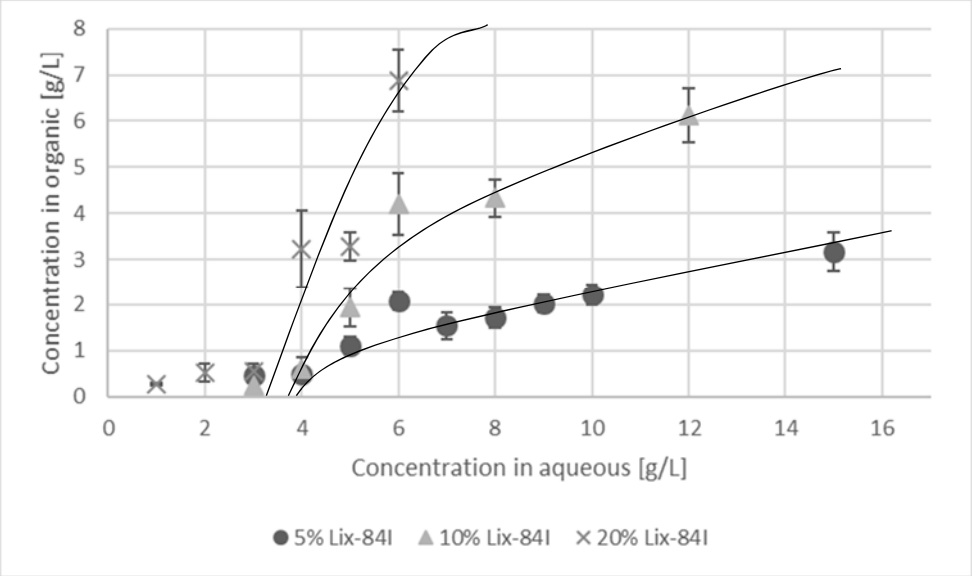

Figure 4.7: equilibrium isotherms for copper extraction with LIX-84I

The figure above shows that a 20% LIX-84I concentration has a more favourable isotherm compared to 10% and 5%. A threshold concentration of copper in the aqueous phase for all the LIX-84I concentrations was observed, beyond this point no further extraction took place in subsequent extraction stages. This is in contradiction with what Tanda (2017) reported. He reported that 100% extraction of copper from a glycine leach liquor is possible with 5% LIX-84I. Using a leach solution containing 2g/L of copper and a 3:1 ratio of glycine to copper, coming to 0.095M, 15 times lower than used in this study.

Rewriting equation [2.20] in terms of an equilibrium constant K_{eq} yields equation [4.1]. From with it is evident that the ratio of available glycine and extractant increases after each extraction where equilibrium is reached. The initial extractant concentration [RH] is constant in

subsequent extractions, the copper glycinate complex $[Cu(H_2NCH_2COO)_2]$ concentration is however significantly lower. The denominator of the equilibrium equation is thus smaller. The numerator is however larger as a result of the increased glycine concentration. With K_{eq} constant, a higher glycine concentration and lower copper glycinate concentration one can deduct that the organometallic complex concentration should be low to satisfy the equilibrium equation. This also explains why the minimum concentration reached is lower for higher concentrations of the extractant. This minimum threshold is at 2.1g/L, 3g/L and 4g/L for 20%, 10% and 5% solutions of LIX-84I respectively.

$$K_{eq} = \frac{[H_2NCH_2COOH]^2[R_2Cu]}{[RH]^2[Cu(H_2NCH_2COO)_2]} = \frac{[GlyH]^2[R_2Cu]}{[RH]^2[Cu(Gly)_2]} \quad [4.1]$$

McCabe-Thiele for the extraction of copper from the PLS using 20% LIX-84I at a pH of 10 for various A:O ratios are shown in Chapter 5.

4.2.5 Stripping

Three large batches of loaded organic extractant were prepared for stripping tests. These batches were prepared from pH 10 PLS and using 20% LIX-84I at a 1:1 A:O ratio. Stripping of the loaded organic phase was investigated using sulphuric acid with varying concentrations from 0.5M to 3M. The A:O ratio was also varied to obtain more equilibrium points for the stripping isotherm and to determine an upper limit to copper concentration in the concentrated electrolyte. Figure 4.8 shows the percentage recovery of copper from the loaded organic phase versus the O:A ratio and figure 4.9 the concentration of copper in the acid versus the O:A ratio. 0.5M sulphuric acid was only able to strip 72% of the copper from the loaded organic phase at a 1:1 ratio and this decreased to 30% at a 4:1 O:A ratio. At 1M sulphuric acid, 95% of the copper was stripped at a 1:1 ratio, this then linearly declined to 80% at a O:A ratio of 4:1. 2M and 3M sulphuric acid showed very similar extractions, 100% of the copper was extracted at O:A ratios of up to 4:1 and 80% was extracted at a 6:1 ratio. The highest equilibrium copper concentration with 0.5M was 7.8g/L, 21g/L for 1M and 30g/L for both 2 and 3M.

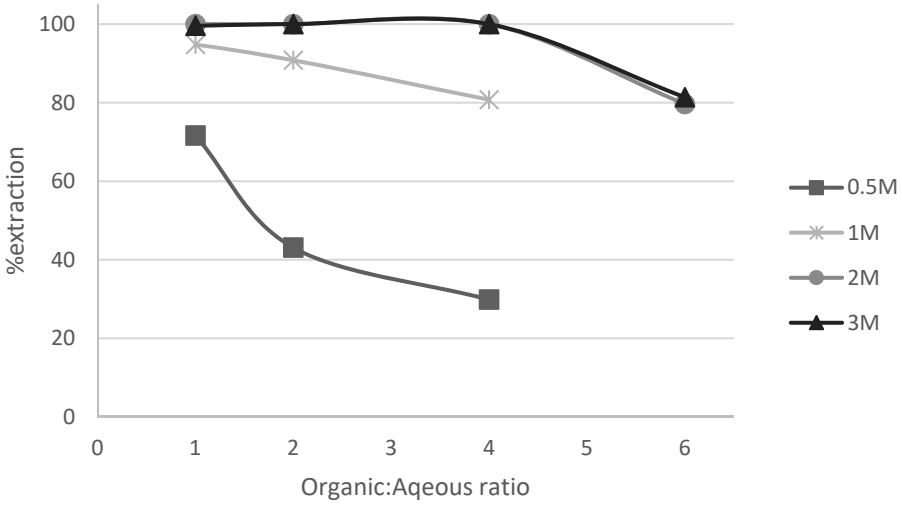

Figure 4.8: Percentage recovery of copper from loaded organic phase

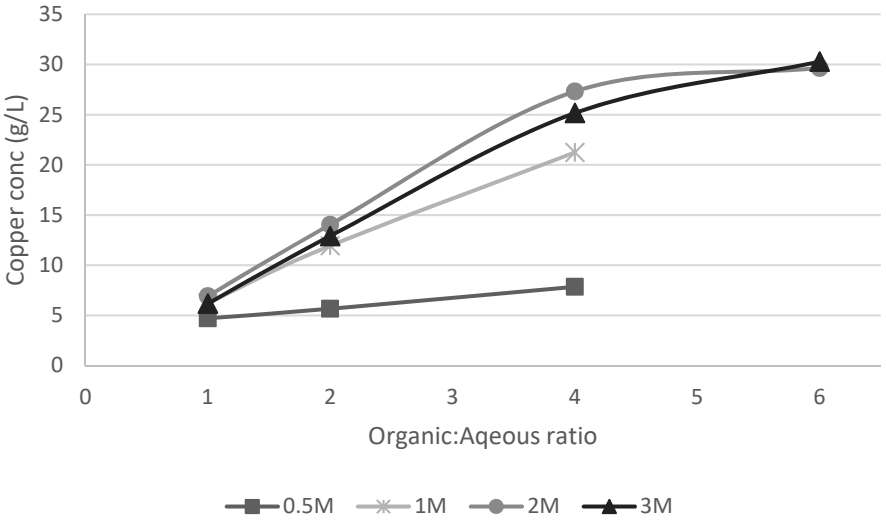

Figure 4.9: Copper concentration in concentrated electrolyte

4.10 shows the stripping isotherm for 2M sulphuric acid from the loaded organic phase. Copper concentrations of up to 12g/L can be stripped of all the copper in a single stage using a 2:1 O:A ratio.

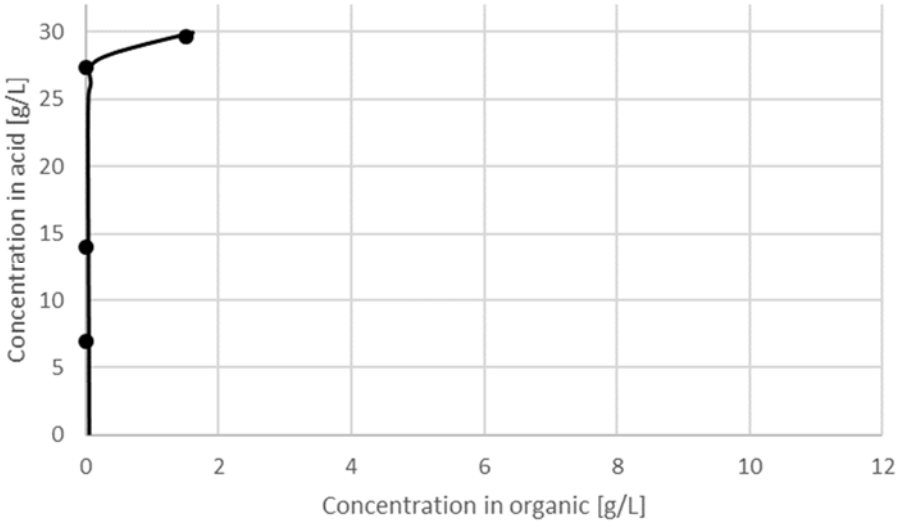

Figure 4.10: Stripping isotherm for 2M sulphuric acid from 20% LIX-84I

4.2.6 Fate of glycine during extraction

The fate of glycine during the extractions was evaluated using ninhydrin test. The ninhydrin reacts with the free amines of the amino acid at elevated temperatures and forms a deep purple, known as Ruhemann's purple. The absorbance of light at a wavelength of 570nm is an indication of the concentration of the Ruhemann's purple and thus glycine concentration. Samples from glycine solutions containing no metals and PLS before and after contact with LIX-84I solutions were tested.

No difference in the absorbance for both test samples were found and it can be concluded that the glycine is not co-extracted. Tanda (2017) found the same results using high performance liquid chromatography.

4.2.7 Conclusion

Solvent extraction using LIX-84I can successfully be applied to recover copper from an alkaline glycine leach liquor. pH values ranging from 8 to 11 were evaluated and extractant concentrations between 5 and 20%. The PLS contained 10g/L copper, 1.5g/L lead and 1.1g/L zinc. LIX-84I is highly selective for copper at the conditions tested. No co-extraction of any other metals was found at any of the conditions. Increasing the pH of the aqueous phase improved the recovery of copper from 64 to 86% in a single stage with a 20% solution of LIX-84I. Increasing the solvent concentration from 5 to 20% at a pH of 10 showed an almost linear increase in the recovery, the recovery increased from 17% at a 5% LIX-84I concentration and to 64% at a 20% LIX-84I concentration. Equilibrium isotherms were drawn for 5, 10 and 20%

LIX-84I concentrations and showed that 80% copper recovery is possible with 2 stages from a PLS containing 10g/L of copper at a A:O ratio of 2:1. 2M sulphuric acid can successfully strip 100% of the copper from a loaded organic phase with O:A ratios of up to 4:1, resulting in a final copper concentration of 22g/L in the concentrated electrolyte. No glycine was co-extracted during the solvent extraction stages.

5 FLOWSHEET DEVELOPMENT

A flowsheet to recover copper from a glycine leach liquor using solvent extraction was developed. It was assumed that the leach liquor had a similar composition to what was used in the study as shown in table 3.4. The flowsheet is based on using a 20% solution of LIX-84I at a pH of 10.

5.1 McCabe-Thiele constructions

The McCabe-Thiele plots for A:O ratios of 3:1 and 2:1 respectively are shown in figures 5.1 and 5.2. With an A:O of 3:1 a raffinate concentration of approximately 3.8g/L can be obtained with 2 stages. At an A:O of 2:1 the raffinate concentration is slightly higher, around 4g/L.

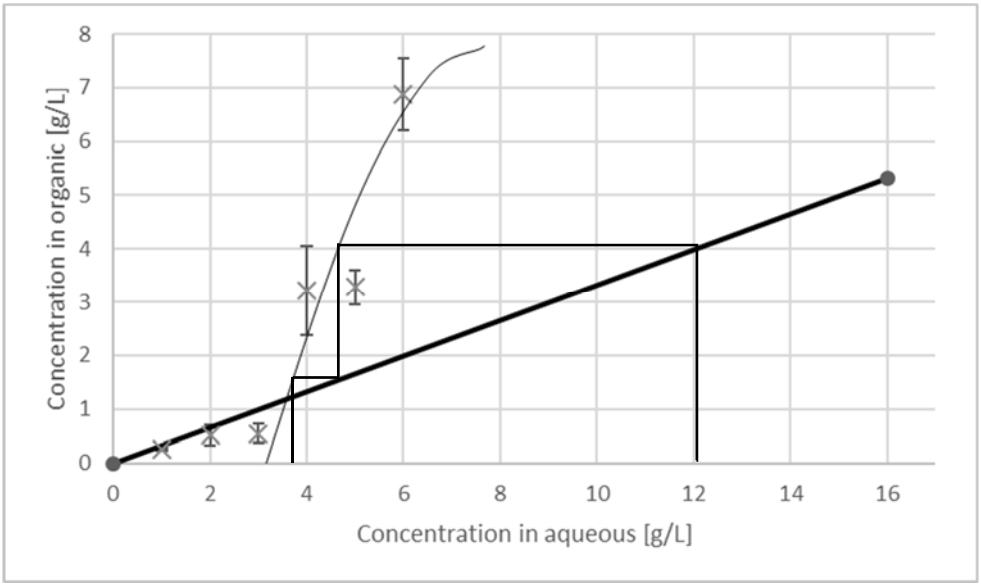

Figure 5.1: McCabe-Thiele for 20% LIX-84I at A:O of 3:1

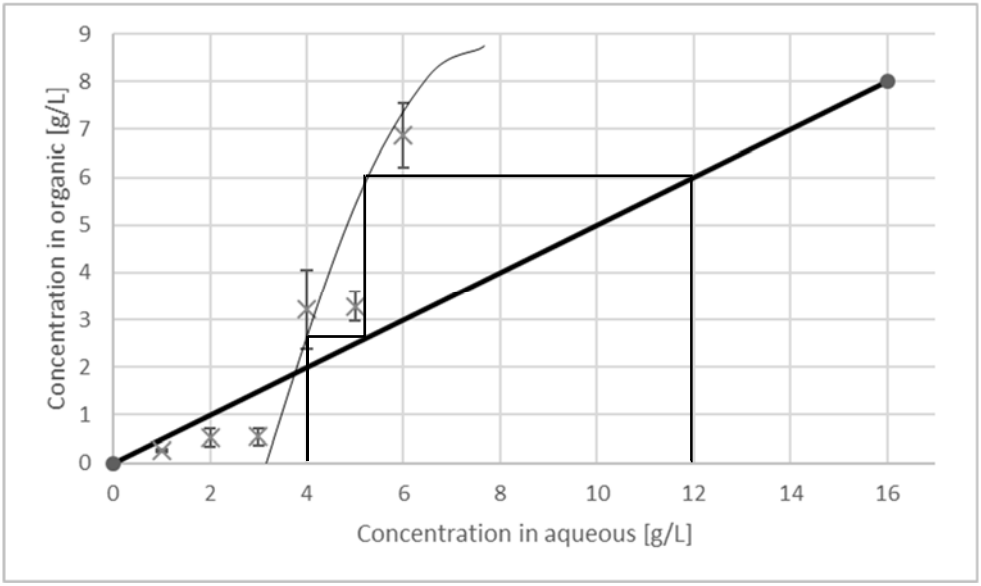

Figure 5.2: McCabe-Thiele for 20% LIX-84I at A:O of 2:1

Assuming that the organic feed contains no copper can be validated by choosing the correct stripping conditions as discussed in section 4.2.5. The concentrations in the loaded organic can be estimated with a mass balance as shown in table 5.1. Decreasing the A:O ratio does not have significant effect on the extraction, but it does lower the concentration of copper in the organic phase from 4g/L to 2.7g/L. An A:O ratio of 1:2 will thus be used for the flowsheet.

Table 5.1: Extraction mass balance from McCabe-Thiele

	Concentration [g/L]			
A:O	**PLS**	**Raffinate**	**Stripped organic**	**Loaded organic**
1:3	12	3.8	0	2.73
1:2	12	4	0	4

Figure 5.3 shows the McCabe-Thiele construction for the stripping phase using 2M sulphuric acid at an acid to organic ratio of 1:3. It was assumed that the spend electrolyte contains 10g/L of copper after returning from solid copper recovery.

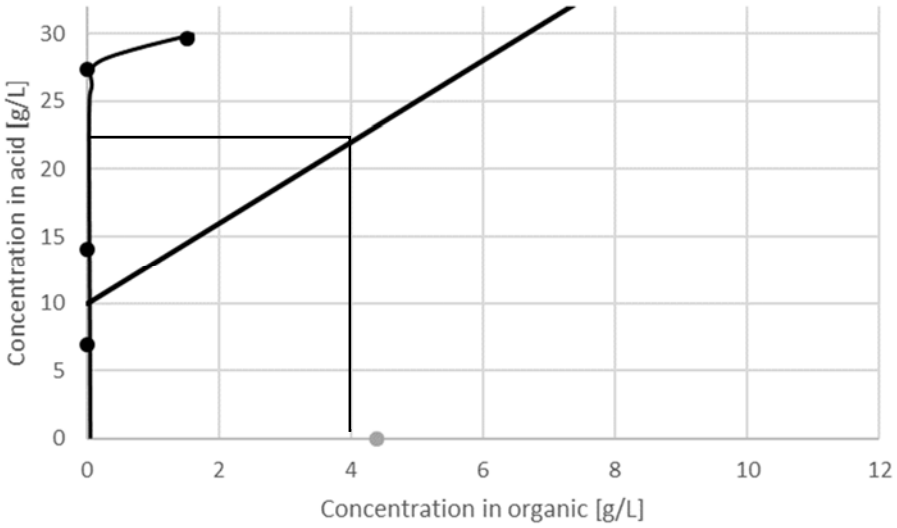

Figure 5.3: McCabe-Thiele for stripping using 2M sulphuric acid at A:O of 1:3

This equates to a copper concentration of 22g/L in the concentrated electrolyte.

Figure 5.4 shows a proposed flowsheet for the recovery of copper from a glycine PLS using 20% LIX-84I and 2M sulphuric acid.

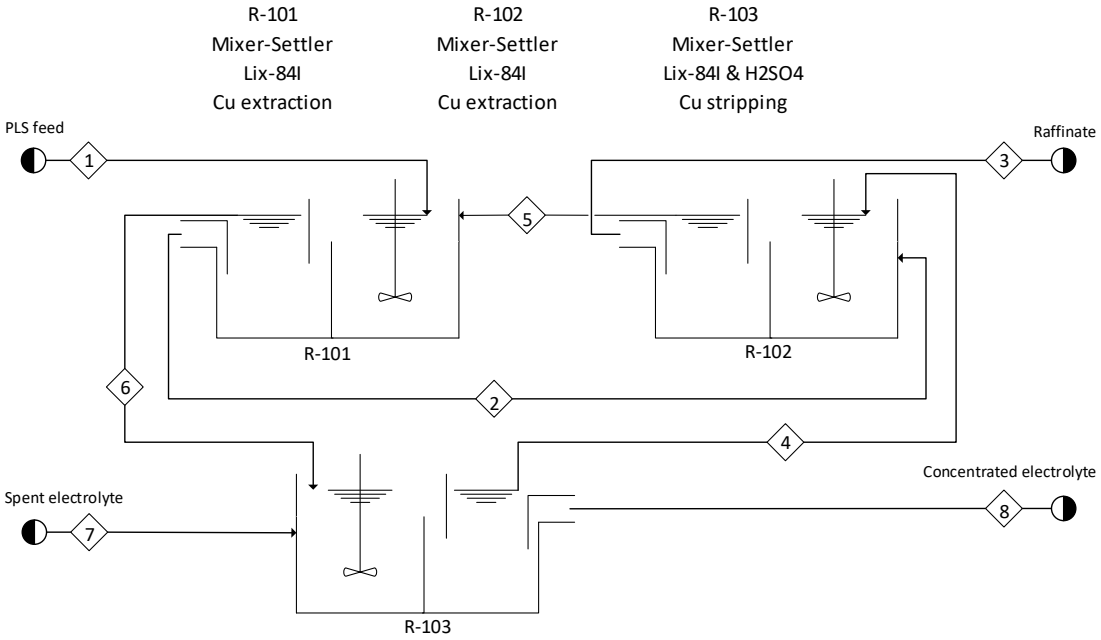

Figure 5.4: Flowsheet for solvent extraction circuit.

Table 5.1 shows the stream table for the proposed flowsheet. A base flowrate of 100kg/h was chosen for the PLS feed.

Table 5.2: Stream table

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Flowrate [L/h]	100	100	100	200	200.0	200.0	66.7	66.7
Component concentration [g/L]								
Al	0.3	0.3	0.3	0	0	0	0	0
Cu	12	5.2	4	0	3.4	4	10	22
Fe	0	0	0	0	0	0	0	0
Ni	0	0	0	0	0	0	0	0
Pb	1.2	1.2	1.2	0	0	0	0	0
Sn	0	0	0	0	0	0	0	0
Zn	1	1	1	0	0	0	0	0
LIX-84I	-	-	-	20%	20%	20%	-	-
H2SO4 [M]	-	-	-	-	-	-	2	2

The proposed process can extract 66% of the copper present in the PLS and raise the concentration from 12g/L in the PLS to 23.2g/L in the concentrated electrolyte.

6 SUMMARY AND CONCLUSION

Solvent extraction and ion exchange were investigated as possible methods to selectively recover copper form an alkaline glycine leach liquor obtained by leaching electronic waste. The leach liquor contained 10g/L copper, 1.5g/L lead and 1.1g/L zinc. It was found that solvent extraction using LIX-84I can successfully be applied to recover copper from an alkaline glycine leach liquor. pH values ranging from 8 to 11 were evaluated and solvent concentrations between 5 and 20%. LIX-84I is highly selective for copper at the conditions tested. No co-extraction of any other metals was found at any of the conditions. Increasing the pH of the aqueous phase improved the recovery of copper from 64 to 86% in a single stage with a 20% solution of LIX-84I. Increasing the solvent concentration from 5 to 20% at a pH of 10 showed an almost linear increase in the recovery, the recovery increased from 17% with a 5% LIX-84I concentration and to 64% with a 20% LIX-84I concentration. Equilibrium isotherms were drawn for 5, 10 and 20% LIX-84I concentrations and showed that 80% copper recovery is possible with 2 stages from a PLS containing 10g/L of copper at a A:O ratio of 2:1. 2M sulphuric acid can successfully strip 100% of the copper from a loaded organic phase with O:A ratios of up to 4:1, resulting in a final copper concentration of 27g/L in the concentrated electrolyte. The fate of glycine during the solvent extraction was tested using UV-VIS and it was confirmed that no glycine was extracted to the organic phase.

Copper recovery from the glycine PLS was proven to be ineffective using commercially available ion exchangers. Both iminodiacetic acid resins tested, S930Plus and TP207, showed no selectivity of copper over lead or zinc at the conditions that were tested. The separation factors found were 0.03 and 0.02 for copper over lead and zinc respectively with S930Plus, for TP207 the values were 0.04 and 0.02 for copper over lead and zinc respectively. S930Plus had equilibrium resin concentration of 11.7g/L copper, 9.1g/L lead and 6.7g/L zinc, and TP207 showed equilibrium concentrations of 16.1g/L copper, 10.5g/L lead and 7.8g/L zinc. Column elution tests showed that all the metals are removed at a similar rate indicating that split elution would also not be an option for the purification of copper. The concentrations found in the eluate were 5.5g/L coper, 4.7g/L lead and 3.2g/L zinc from S930Plus and 8g/L copper, 6.2/L lead and 5.2g/L zinc from TP207. The bis-picolylamine resins tested, TP220, showed separation factors of 1.67 and 1.40 for copper over lead and zinc respectively, these values are relatively close to 1 and effective separation of the metals was not achieved, the equilibrium concentrations were, 6.1g/L for copper, 0.9g/L lead and 0.8g/L zinc.

A solvent extraction process that is able to selectively recover 66% of the copper present in the pregnant leach solution was proposed. The copper concentration in the final concentrated electrolyte was 22g/L.

7 RECOMMENDATIONS FOR FUTURE WORK

The following recommendations for future work are made:

- Investigate the effect of flowrate and acid concentration on the elution of ion exchange resins, to evaluate if split elution might be possible.
- Construct equilibrium isotherms for LIX-84I at single stage extractions using higher A:O ratios to investigate the effect of free glycine in the aqueous phase. Using lower pulp densities for the leaching phase would also allow for lower glycine concentrations.
- Perform larger scale continuous solvent extraction tests to evaluate the ability of LIX-84I to be used in a continuous industrial process.
- Investigate the removal of lead and zinc from the raffinate prior to recycling to reduce the build-up of impurities.

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APPENDIX A : DATA VALIDATION

A-1: Ion exchange mass balances and repeatability

A complete mass balance reconciliation was performed for S930Plus and TP207. The concentration of the metals present in the initial PLS was tested, together with the concentration after the 24h stirred beaker tests. The eluate was also analysed for their metal content and the mass balance could be closed. Table A-1 shows the overall mass balance for S930Plus and A-2 how the total metal in the eluate was calculated. The mass balances closed with less than 10% error for both resins. Repeatability was tested using TP207, the AAS was used to analyse the sample, and there was only tested for copper. The results are shown in Table A.5 and Table A.6 . The repeatability was proven to be good, there was minimal difference between the two tests.

Table A.1: S930Plus mass balance

	PLS conc [g/L]	Raffinate conc [g/L]	PLS volume [mL]	Mass in PLS [g]	Mass in raffinate [g]	Mass in eluate [g]	Total mass before exchange [g]	Total mass after exchange [g]	%error
Al	0.01	0.01	250	0.00	0.00	0.00	0.00	0.00	6.19%
Cu	5.20	2.86	250	1.30	0.72	0.52	1.30	1.23	5.26%
Fe	0.02	0.02	250	0.01	0.00	0.00	0.01	0.01	6.78%
Ni	0.01	0.00	250	0.00	0.00	0.00	0.00	0.00	3.18%
Pb	1.89	0.06	250	0.47	0.02	0.44	0.47	0.46	2.99%
Sn	0.00	0.00	250	0.00	0.00	0.00	0.00	0.00	4.46%
Zn	1.41	0.03	250	0.35	0.01	0.32	0.35	0.33	6.76%

Table A.2: Elution table for S930Plus

	Sample tube nr.	1	2	3	4	5	6	7	8	9	10	Total
Concentration [g/L]	**Al**	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	-
	Cu	0.00	0.99	4.05	4.47	5.82	3.46	2.45	1.33	0.37	0.01	-
	Fe	0.00	0.00	0.01	0.01	0.02	0.01	0.01	0.00	0.00	0.00	-
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
	Pb	0.00	0.89	3.60	3.99	4.84	2.96	1.96	1.03	0.26	0.01	-
	Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
	Zn	0.00	1.08	2.84	3.12	3.10	1.96	1.14	0.53	0.14	0.05	-
Mass in sample [g]	**Volume [mL]**	5	26	25	25	18	23	20	26	27	25	-
	Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Cu	0.00	0.03	0.10	0.11	0.10	0.08	0.05	0.03	0.01	0.00	0.52
	Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Pb	0.00	0.02	0.09	0.10	0.09	0.07	0.04	0.03	0.01	0.00	0.44
	Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Zn	0.00	0.03	0.07	0.08	0.06	0.05	0.02	0.01	0.00	0.00	0.32

Table A.3: TP207 mass balance

	PLS conc [g/L]	Raffinate conc [g/L]	PLS volume [mL]	Mass in PLS [g]	Mass in raffinate [g]	Mass in eluate [g]	Total mass before exchange [g]	Total mass after exchange [g]	%error
Al	0.35	0.31	250	0.09	0.08	0.01	0.09	0.08	2.56%
Cu	9.33	6.11	250	2.33	1.53	0.73	2.33	2.26	3.30%
Fe	0.02	0.02	250	0.00	0.00	0.00	0.00	0.00	4.50%
Ni	0.01	0.01	250	0.00	0.00	0.00	0.00	0.00	3.55%
Pb	2.26	0.15	250	0.56	0.04	0.55	0.56	0.59	3.97%
Sn	0.01	0.01	250	0.00	0.00	0.00	0.00	0.00	7.35%
Zn	1.63	0.07	250	0.41	0.02	0.44	0.41	0.45	9.89%

Table A.4: Elution table for TP207

	Sample tube nr.	1	2	3	4	5	6	7	8	9	10	Total
Concentration [g/L]	**Al**	0.01	0.07	0.07	0.05	0.02	0.02	0.01	0	0	0	-
	Cu	1.01	7.45	8.16	6.79	1.86	2.84	0.83	0.13	0.07	0.02	-
	Fe	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	-
	Ni	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	-
	Pb	0.75	5.68	6.27	5.06	1.51	2.04	0.51	0.09	0.05	0.01	-
	Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
	Zn	0.97	5.34	4.84	3.37	1.12	1.55	0.19	0.04	0.02	0.01	-
Mass in sample [g]	**Volume [mL]**	25	25	25	25	25	25	25	25	25	25	-
	Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	Cu	0.03	0.19	0.20	0.17	0.05	0.07	0.02	0.00	0.00	0.00	0.73
	Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Pb	0.02	0.14	0.16	0.13	0.04	0.05	0.01	0.00	0.00	0.00	0.55
	Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Zn	0.02	0.13	0.12	0.08	0.03	0.04	0.00	0.00	0.00	0.00	0.44

Table A.5: Repeatability results TP207

	PLS conc [g/L]	Raffinate conc [g/L]	PLS volume [mL]	Mass in PLS [g]	Mass in raffinate [g]	Mass in eluate [g]	Total mass before exchange [g]	Total mass after exchage [g]	%error
1st	9.33	6.11	250	2.33	1.53	0.73	2.33	2.26	3.30%
2nd	9.65	6.01	250	2.41	1.50	0.77	2.41	2.27	5.78%

Table A.6: Elution repeatability results TP207

Sample tube nr.	1	2	3	4	5	6	7	8	9	10	Total
1st [g/L]	1.01	7.45	8.16	6.79	1.86	2.84	0.83	0.13	0.07	0.02	-
2nd [g/L]	0.00	5.03	5.54	4.82	4.73	6.09	3.50	0.78	0.37	0.00	-
Volume [mL]	25	25	25	25	25	25	25	25	25	25	-
1st [g]	0.03	0.19	0.20	0.17	0.05	0.07	0.02	0.00	0.00	0.00	0.73
2nd [g]	0.00	0.13	0.14	0.12	0.12	0.15	0.09	0.02	0.01	0.00	0.77

A-2: Solvent extraction mass balances and repeatability

A mass balance reconciliation for the solvent extraction experimental work was performed. Table A.7 shows the result for the tests performed using 10% LIX-84I, pH10 and A:O 1:1. Only the results for copper are shown in the table as no other metals were co-extracted. It is evident that the mass balance closes. This was found to be true for all of the data obtained.

Table A.7: Mass balance for 10% LIX-84I, pH10 and A:O 1:1

PLS conc [g/L]	Raffinate conc [g/L]	PLS vol [mL]	Mass in PLS [g]	Mass in raffinate [g]	Acid conc [g/L]	Acid vol [mL]	Mass in acid [g]	Total mass before [g]	Total mass after [g]	%error
17.38	13.60	100	1.74	1.36	4.50	100	0.45	1.74	1.81	3.99%
18.03	11.88	100	1.80	1.19	6.10	100	0.61	1.80	1.80	0.24%
12.03	7.86	75	0.90	0.59	4.48	75	0.34	0.90	0.93	2.53%
10.17	6.19	50	0.51	0.31	4.17	50	0.21	0.51	0.52	1.81%
6.19	4.38	46	0.28	0.20	1.54	46	0.07	0.28	0.27	4.25%
4.38	3.75	43	0.19	0.16	0.39	43	0.02	0.19	0.18	5.50%

APPENDIX B : EXPERIMENTAL DATA

B-1: Ion exchange data

Table B.1: Ion exchange stirred beaker data

			Conc g/L							Resin conc [g/L]						
	L:R ratio	Time (hours)	Al	Cu	Fe	Ni	Pb	Sn	Zn	Al	Cu	Fe	Ni	Pb	Sn	Zn
S930 Plus 1:50	**50**	**0**	0.01	5.36	0.02	0.02	1.77	0.01	1.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	50	**0.5**	0.01	5.33	0.02	0.01	1.36	0.00	1.15	0.00	1.82	0.00	0.50	20.66	0.09	4.73
	50	**1**	0.01	5.25	0.02	0.01	1.32	0.00	1.17	0.00	5.68	0.00	0.57	22.72	0.09	3.71
	50	**2**	0.01	5.07	0.02	0.01	1.17	0.00	1.11	0.00	14.65	0.00	0.60	29.79	0.12	6.95
	50	**4**	0.01	5.02	0.02	0.01	1.06	0.00	1.10	0.00	16.98	0.00	0.62	35.34	0.13	7.43
	50	**8**	0.01	5.16	0.02	0.01	1.01	0.00	1.11	0.00	10.41	0.00	0.63	37.90	0.12	6.70
	50	**12**	0.01	5.25	0.02	0.01	1.00	0.00	1.14	0.00	5.59	0.00	0.64	38.40	0.19	5.29
	50	**24**	0.01	5.24	0.02	0.01	0.96	0.00	1.13	0.00	6.30	0.00	0.64	40.31	0.11	5.81
S930 Plus 1:25	**25**	**0**	0.01	5.37	0.02	0.01	1.94	0.00	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	25	**0.5**	0.01	4.54	0.02	0.01	0.97	0.00	0.99	0.00	20.76	0.04	0.00	24.14	0.00	10.93
	25	**1**	0.01	4.50	0.02	0.01	0.90	0.00	0.94	0.01	21.62	0.05	0.01	25.95	0.00	12.06
	25	**2**	0.01	4.52	0.02	0.01	0.80	0.00	0.89	0.01	21.02	0.01	0.01	28.44	0.00	13.40
	25	**4**	0.01	4.55	0.02	0.01	0.69	0.00	0.82	0.01	20.36	0.03	0.02	31.10	0.00	15.19
	25	**8**	0.01	4.67	0.02	0.01	0.64	0.00	0.79	0.00	17.27	0.02	0.01	32.53	0.02	15.90
	25	**12**	0.01	4.81	0.02	0.01	0.61	0.00	0.80	0.00	13.76	0.01	0.01	33.23	0.00	15.66
	25	**24**	0.01	4.99	0.02	0.01	0.56	0.00	0.81	0.00	9.31	0.00	0.00	34.38	0.01	15.48
S930 Plus 1:5	**5**	**0**	0.01	5.20	0.02	0.01	1.89	0.00	1.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	**0.5**	0.01	3.11	0.02	0.01	0.48	0.01	0.22	0.00	10.46	0.01	0.00	7.03	0.00	5.92
	5	**1**	0.01	3.09	0.02	0.01	0.39	0.01	0.16	0.00	10.58	0.01	0.00	7.49	0.00	6.23
	5	**2**	0.01	2.62	0.02	0.01	0.20	0.02	0.08	0.00	12.92	0.00	0.01	8.46	0.00	6.62
	5	**4**	0.01	2.75	0.02	0.01	0.11	0.01	0.06	0.00	12.25	0.01	0.01	8.89	0.00	6.72
	5	**8**	0.01	2.78	0.02	0.01	0.08	0.01	0.04	0.00	12.12	0.02	0.01	9.03	0.00	6.81

			Conc g/L							Resin conc [g/L]						
	L:R ratio	Time (hours)	Al	Cu	Fe	Ni	Pb	Sn	Zn	Al	Cu	Fe	Ni	Pb	Sn	Zn
	5	**12**	0.01	2.74	0.02	0.00	0.08	0.02	0.04	0.00	12.29	0.00	0.01	9.05	0.00	6.83
	5	**24**	0.01	2.86	0.02	0.00	0.06	0.01	0.03	0.00	11.70	0.02	0.01	9.11	0.00	6.86
TP220 1:50	**50**	**0**	0.38	9.90	0.02	0.01	2.29	0.01	1.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	50	**0.5**	0.38	9.70	0.02	0.01	2.28	0.01	1.65	0.34	9.67	0.01	0.01	0.28	0.02	0.00
	50	**1**	0.39	10.12	0.02	0.01	2.37	0.01	1.71	0.00	0.00	0.00	0.00	0.00	0.06	0.00
	50	**2**	0.38	9.92	0.02	0.01	2.32	0.00	1.68	0.09	0.00	0.01	0.01	0.00	0.09	0.00
	50	**4**	0.39	10.03	0.02	0.01	2.36	0.01	1.70	0.00	0.00	0.00	0.01	0.00	0.02	0.00
	50	**8**	0.40	10.25	0.02	0.01	2.41	0.01	1.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	50	**12**	0.39	10.11	0.02	0.01	2.38	0.01	1.72	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	50	**24**	0.42	10.71	0.02	0.01	2.55	0.01	1.83	0.00	0.00	0.00	0.00	0.00	0.02	0.00
TP220 1:25	**25**	**0**	0.40	10.32	0.02	0.01	2.43	0.01	1.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	25	**0.5**	0.37	9.60	0.02	0.01	2.29	0.00	1.64	0.78	17.99	0.00	0.01	3.46	0.03	2.70
	25	**1**	0.38	9.96	0.02	0.01	2.35	0.01	1.68	0.42	8.97	0.00	0.00	2.12	0.01	1.52
	25	**2**	0.38	9.74	0.02	0.01	2.29	0.01	1.65	0.61	14.43	0.01	0.01	3.53	0.00	2.46
	25	**4**	0.39	10.10	0.02	0.01	2.36	0.01	1.71	0.22	5.59	0.00	0.00	1.70	0.00	1.00
	25	**8**	0.39	9.94	0.02	0.01	2.32	0.01	1.68	0.34	9.66	0.00	0.01	2.72	0.00	1.70
	25	**12**	0.39	9.97	0.02	0.01	2.34	0.01	1.68	0.32	8.71	0.01	0.01	2.39	0.01	1.60
	25	**24**	0.40	10.11	0.02	0.01	2.37	0.01	1.71	0.16	5.29	0.00	0.01	1.64	0.00	1.01
TP220 1:5	**5**	**0**	0.36	9.61	0.02	0.01	2.32	0.01	1.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	**0.5**	0.32	8.21	0.02	0.01	2.05	0.01	1.45	0.18	7.01	0.00	0.01	1.37	0.00	1.15
	5	**1**	0.31	7.96	0.02	0.01	1.99	0.01	1.41	0.23	8.24	0.00	0.01	1.65	0.00	1.35
	5	**2**	0.30	7.83	0.02	0.01	1.94	0.01	1.38	0.27	8.91	0.00	0.01	1.89	0.00	1.47
	5	**4**	0.30	7.83	0.02	0.01	1.94	0.01	1.38	0.27	8.91	0.00	0.01	1.89	0.00	1.48
	5	**8**	0.31	7.97	0.02	0.01	1.99	0.01	1.42	0.24	8.19	0.00	0.01	1.67	0.00	1.29
	5	**12**	0.31	7.97	0.02	0.01	1.98	0.01	1.41	0.23	8.19	0.00	0.01	1.68	0.00	1.32
	5	**24**	0.33	8.38	0.02	0.01	2.13	0.01	1.52	0.12	6.15	0.00	0.01	0.93	0.00	0.79
TP 20	**50**	**0**	0.36	9.55	0.02	0.01	2.31	0.01	1.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00

			Conc g/L							Resin conc [g/L]						
	L:R ratio	Time (hours)	Al	Cu	Fe	Ni	Pb	Sn	Zn	Al	Cu	Fe	Ni	Pb	Sn	Zn
	50	**0.5**	0.37	9.02	0.02	0.01	1.90	0.01	1.49	0.00	26.58	0.01	0.00	20.64	0.00	8.77
	50	**1**	0.35	8.43	0.02	0.01	1.62	0.01	1.36	0.49	55.96	0.01	0.02	34.85	0.00	15.65
	50	**2**	0.38	9.24	0.02	0.01	1.61	0.01	1.43	0.00	15.54	0.00	0.01	35.37	0.00	11.74
	50	**4**	0.38	9.68	0.02	0.01	1.50	0.01	1.46	0.00	0.00	0.00	0.00	40.57	0.00	10.50
	50	**8**	0.38	9.37	0.02	0.01	1.40	0.01	1.41	0.00	8.96	0.01	0.01	45.83	0.00	12.91
	50	**12**	0.38	9.32	0.02	0.01	1.38	0.01	1.39	0.00	11.58	0.00	0.00	46.59	0.00	13.87
	50	**24**	0.39	9.58	0.02	0.01	1.40	0.01	1.42	0.00	0.00	0.00	0.00	45.55	0.00	12.65
TP207 1:25	**25**	**0**	0.35	9.52	0.02	0.01	2.30	0.01	1.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	25	**0.5**	0.35	8.41	0.02	0.01	1.55	0.01	1.31	0.06	27.62	0.03	0.01	18.71	0.00	8.70
	25	**1**	0.36	8.46	0.02	0.01	1.31	0.01	1.22	0.00	26.32	0.02	0.00	24.52	0.00	11.01
	25	**2**	0.37	8.88	0.02	0.01	1.17	0.00	1.18	0.00	15.91	0.02	0.00	28.23	0.03	11.96
	25	**4**	0.37	9.13	0.02	0.01	1.00	0.01	1.13	0.00	9.59	0.02	0.00	32.35	0.00	13.11
	25	**8**	0.37	8.87	0.02	0.01	0.86	0.01	1.06	0.00	16.19	0.02	0.00	35.85	0.01	14.96
	25	**12**	0.38	8.88	0.02	0.01	0.87	0.01	1.09	0.00	15.87	0.01	0.00	35.58	0.00	14.20
	25	**24**	0.41	8.90	0.02	0.01	0.92	0.01	1.13	0.00	15.31	0.01	0.00	34.42	0.00	13.10
TP207 1:5	**5**	**0**	0.35	9.33	0.02	0.01	2.26	0.01	1.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	**0.5**	0.30	6.01	0.02	0.01	0.59	0.01	0.47	0.24	16.62	0.00	0.00	8.32	0.00	5.81
	5	**1**	0.30	5.81	0.02	0.01	0.40	0.01	0.25	0.23	17.64	0.01	0.00	9.28	0.00	6.91
	5	**2**	0.30	5.77	0.02	0.01	0.30	0.01	0.16	0.22	17.80	0.01	0.00	9.79	0.00	7.38
	5	**4**	0.31	5.92	0.02	0.01	0.23	0.01	0.11	0.20	17.08	0.01	0.00	10.14	0.00	7.63
	5	**8**	0.30	5.84	0.02	0.01	0.17	0.01	0.08	0.22	17.45	0.01	0.00	10.42	0.00	7.77
	5	**12**	0.31	6.00	0.02	0.01	0.17	0.01	0.07	0.18	16.65	0.00	0.00	10.44	0.00	7.79
	5	**24**	0.31	6.11	0.02	0.01	0.15	0.01	0.07	0.17	16.11	0.01	0.00	10.53	0.00	7.83

Table B.2: Resin elution data

			Conc g/L							Mass of metal in sample (g)							Cumulative mass removed (g)						
	Volume	**Nr**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**
S930 plus	**5**	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	26	2	0.00	0.99	0.00	0.00	0.89	0.00	1.08	0.00	0.03	0.00	0.00	0.02	0.00	0.03	0.00	0.03	0.00	0.00	0.02	0.00	0.03
	25	3	0.01	4.05	0.01	0.00	3.60	0.00	2.84	0.00	0.10	0.00	0.00	0.09	0.00	0.07	0.00	0.13	0.00	0.00	0.11	0.00	0.10
	25	4	0.01	4.47	0.01	0.00	3.99	0.00	3.12	0.00	0.11	0.00	0.00	0.10	0.00	0.08	0.00	0.24	0.00	0.00	0.21	0.00	0.18
	18	5	0.01	5.44	0.02	0.00	4.67	0.00	3.15	0.00	0.10	0.00	0.00	0.08	0.00	0.06	0.00	0.34	0.00	0.00	0.30	0.00	0.23
	23	6	0.01	3.46	0.01	0.00	2.96	0.00	1.96	0.00	0.08	0.00	0.00	0.07	0.00	0.05	0.00	0.42	0.00	0.00	0.37	0.00	0.28
	20	7	0.00	2.45	0.01	0.00	1.96	0.00	1.14	0.00	0.05	0.00	0.00	0.04	0.00	0.02	0.00	0.47	0.00	0.00	0.40	0.00	0.30
	26	8	0.00	1.33	0.00	0.00	1.03	0.00	0.53	0.00	0.03	0.00	0.00	0.03	0.00	0.01	0.00	0.50	0.00	0.00	0.43	0.00	0.32
	27	9	0.00	0.37	0.00	0.00	0.26	0.00	0.14	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.51	0.00	0.00	0.44	0.00	0.32
	25	10	0.00	0.01	0.00	0.00	0.01	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00	0.00	0.44	0.00	0.32
TP 207	**25**	1	0.01	1.01	0.00	0.00	0.75	0.00	0.97	0.00	0.03	0.00	0.00	0.02	0.00	0.02	0.00	0.03	0.00	0.00	0.02	0.00	0.02
	25	2	0.07	7.45	0.00	0.01	5.68	0.00	5.34	0.00	0.19	0.00	0.00	0.14	0.00	0.13	0.00	0.21	0.00	0.00	0.16	0.00	0.16
	25	3	0.07	8.16	0.01	0.01	6.27	0.00	4.84	0.00	0.20	0.00	0.00	0.16	0.00	0.12	0.00	0.42	0.00	0.00	0.32	0.00	0.28
	25	4	0.05	6.79	0.01	0.01	5.06	0.00	3.37	0.00	0.17	0.00	0.00	0.13	0.00	0.08	0.01	0.59	0.00	0.00	0.44	0.00	0.36
	25	5	0.02	1.86	0.00	0.00	1.51	0.00	1.12	0.00	0.05	0.00	0.00	0.04	0.00	0.03	0.01	0.63	0.00	0.00	0.48	0.00	0.39
	25	6	0.02	2.84	0.00	0.00	2.04	0.00	1.55	0.00	0.07	0.00	0.00	0.05	0.00	0.04	0.01	0.70	0.00	0.00	0.53	0.00	0.43
	25	7	0.01	0.83	0.00	0.00	0.51	0.00	0.19	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.01	0.72	0.00	0.00	0.55	0.00	0.43
	25	8	0.00	0.13	0.00	0.00	0.09	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.73	0.00	0.00	0.55	0.00	0.44
	25	9	0.00	0.07	0.00	0.00	0.05	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.73	0.00	0.00	0.55	0.00	0.44
	25	10	0.00	0.02	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.73	0.00	0.00	0.55	0.00	0.44
TP 220	**25**	1	0.00	0.01	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	25	2	0.04	0.04	0.00	0.00	0.05	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	25	3	0.03	0.05	0.00	0.00	0.04	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	25	4	0.02	0.05	0.00	0.00	0.03	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	25	5	0.02	0.05	0.00	0.00	0.02	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01

			Conc g/L							Mass of metal in sample (g)							Cumulative mass removed (g)						
	Volume	Nr	Al	Cu	Fe	Ni	Pb	Sn	Zn	Al	Cu	Fe	Ni	Pb	Sn	Zn	Al	Cu	Fe	Ni	Pb	Sn	Zn
	25	6	0.02	0.05	0.00	0.00	0.02	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01
	25	7	0.01	0.07	0.00	0.00	0.02	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01
	25	8	0.00	0.10	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.02
	25	9	0.00	0.10	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.02
	25	10	0.00	0.10	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.02

B-2: Solvent extraction data

Table B.3: Solvent extraction ICP data

						Concentration [g/L]						
lix conc	**pH**	**A**	**O**	**PLS**	**vol [mL]**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**
5.00%	10	1	1	Before	50	0.28	10.00	0.00	0.00	1.13	0.01	0.79
5.00%	10	1	1	After 1st	47	0.29	8.32	0.00	0.00	1.36	0.00	1.17
5.00%	10	1	1	After 2nd	43	0.30	6.55	0.00	0.00	1.77	0.00	1.23
5.00%	10	1	1	After 3rd	50	0.30	5.29	0.00	0.00	2.08	0.00	1.25
5.00%	10	1	2	Before	50	0.30	10.45	0.00	0.00	1.38	0.00	1.10
5.00%	10	1	2	After 1st	46	0.28	6.89	0.00	0.00	1.90	0.00	1.19
5.00%	10	1	2	After 2nd	42	0.30	4.44	0.00	0.00	2.47	0.00	1.25
5.00%	10	1	2	After 3rd	100	0.29	3.36	0.00	0.00	2.12	0.00	1.14
5.00%	10	1	4	Before	30	0.29	10.18	0.00	0.00	1.29	0.00	1.02
5.00%	10	1	4	After 1st	27	0.29	5.32	0.00	0.00	2.29	0.00	1.29
5.00%	10	1	4	After 2nd	23	0.27	3.80	0.00	0.00	2.20	0.00	1.15
5.00%	10	1	4	After 3rd	120	0.29	3.73	0.00	0.00	2.14	0.00	1.19
10.00%	10	1	1	Before	50	0.30	10.55	0.00	0.00	1.39	0.00	1.06
10.00%	10	1	1	After 1st	46	0.30	6.26	0.00	0.00	2.03	0.00	1.28
10.00%	10	1	1	After 2nd	43	0.29	4.21	0.00	0.01	2.28	0.00	1.17
10.00%	10	1	1	After 3rd	50	0.32	4.12	0.00	0.00	2.32	0.00	1.27
10.00%	10	1	2	Before	50	0.29	10.42	0.00	0.00	1.32	0.00	1.06
10.00%	10	1	2	After 1st	46	0.34	4.74	0.00	0.00	2.55	0.00	1.35
10.00%	10	1	2	After 2nd	43	0.35	3.70	0.00	0.00	2.42	0.00	1.25
10.00%	10	1	2	After 3rd	100	0.31	3.00	0.00	0.00	2.21	0.00	1.21
10.00%	10	1	4	Before	30	0.29	10.38	0.00	0.00	1.29	0.00	0.87
10.00%	10	1	4	After 1st	26	0.30	5.31	0.00	0.00	1.83	0.00	1.27
10.00%	10	1	4	After 2nd	23	0.27	3.76	0.00	0.01	2.22	0.00	1.20
10.00%	10	1	4	After 3rd	120	0.28	3.44	0.00	0.00	2.00	0.00	1.14
20.00%	10	1	1	Before	50	0.30	10.22	0.00	0.00	1.32	0.00	1.01
20.00%	10	1	1	After 1st	46	0.29	4.48	0.00	0.00	2.40	0.00	1.30
20.00%	10	1	1	After 2nd	43	0.27	2.94	0.00	0.01	2.28	0.00	1.22
20.00%	10	1	1	After 3rd	50	0.27	2.48	0.00	0.00	2.15	0.00	1.21
20.00%	10	1	2	Before	50	0.28	10.34	0.00	0.00	1.23	0.04	1.00
20.00%	10	1	2	After 1st	47	0.27	4.32	0.00	0.00	2.55	0.00	1.34
20.00%	10	1	2	After 2nd	44	0.27	2.83	0.00	0.01	2.15	0.00	1.14
20.00%	10	1	2	After 3rd	100	0.28	2.55	0.00	0.01	2.19	0.00	1.21
20.00%	10	1	4	Before	30	0.29	10.26	0.00	0.00	1.36	0.00	1.02
20.00%	10	1	4	After 1st	27	0.27	3.62	0.00	0.00	2.65	0.00	1.29
20.00%	10	1	4	After 2nd	24	0.29	2.86	0.00	0.01	2.25	0.00	1.22
20.00%	10	1	4	After 3rd	120	0.30	2.76	0.00	0.00	2.24	0.00	1.28
5.00%	11	1	1	Before	50	0.08	10.02	0.04	0.00	0.30	0.01	0.25
5.00%	11	1	1	After 1st	47	0.08	6.50	0.03	0.00	0.30	0.00	0.40
5.00%	11	1	1	After 2nd	44	0.08	4.05	0.03	0.00	0.32	0.00	0.54
5.00%	11	1	1	After 3rd	50	0.08	1.79	0.02	0.00	0.42	0.00	0.66

						Concentration [g/L]						
lix conc	**pH**	**A**	**O**	**PLS**	**vol [mL]**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**
5.00%	11	1	2	Before	50	0.08	8.81	0.04	0.00	0.31	0.00	0.36
5.00%	11	1	2	After 1st	46.5	0.07	4.07	0.02	0.00	0.33	0.00	0.53
5.00%	11	1	2	After 2nd	42.5	0.07	1.23	0.02	0.00	0.67	0.00	0.62
5.00%	11	1	2	After 3rd	100	0.05	0.48	0.02	0.00	0.77	0.00	0.51
5.00%	11	1	4	Before	30	0.08	8.98	0.04	0.00	0.31	0.00	0.32
5.00%	11	1	4	After 1st	27	0.07	1.15	0.02	0.00	0.58	0.00	0.61
5.00%	11	1	4	After 2nd	23.5	0.06	0.59	0.02	0.00	0.77	0.00	0.51
5.00%	11	1	4	After 3rd	120	0.05	0.37	0.02	0.00	0.67	0.00	0.49
10.00%	11	1	1	Before	50	0.08	10.26	0.03	0.00	0.32	0.00	0.46
10.00%	11	1	1	After 1st	47	0.08	4.06	0.02	0.00	0.33	0.00	0.49
10.00%	11	1	1	After 2nd	44	0.07	1.06	0.02	0.00	0.73	0.00	0.55
10.00%	11	1	1	After 3rd	50	0.14	0.42	0.05	0.00	0.80	0.00	0.46
10.00%	11	1	2	Before	50	0.08	8.83	0.03	0.00	0.30	0.00	0.28
10.00%	11	1	2	After 1st	47	0.06	0.91	0.02	0.00	0.62	0.00	0.58
10.00%	11	1	2	After 2nd	43.5	0.04	0.22	0.02	0.00	0.84	0.00	0.52
10.00%	11	1	2	After 3rd	100	0.13	0.15	0.04	0.00	0.68	0.00	0.48
10.00%	11	1	4	Before	30	0.08	9.09	0.04	0.00	0.29	0.00	0.25
10.00%	11	1	4	After 1st	27	0.07	0.88	0.02	0.00	0.49	0.00	0.75
10.00%	11	1	4	After 2nd	23.5	0.04	0.39	0.02	0.00	0.47	0.00	0.48
10.00%	11	1	4	After 3rd	120	0.13	0.28	0.04	0.00	0.50	0.00	0.44
20.00%	11	1	1	Before	50	0.07	10.09	0.03	0.00	0.30	0.00	0.29
20.00%	11	1	1	After 1st	47	0.05	1.38	0.03	0.00	0.56	0.00	0.65
20.00%	11	1	1	After 2nd	43	0.07	0.40	0.03	0.00	0.73	0.00	0.48
20.00%	11	1	1	After 3rd	50	0.03	0.31	0.02	0.00	0.60	0.00	0.47
20.00%	11	1	2	Before	50	0.06	8.61	0.03	0.00	0.28	0.00	0.28
20.00%	11	1	2	After 1st	46	0.03	0.43	0.03	0.00	0.70	0.00	0.56
20.00%	11	1	2	After 2nd	43	0.02	0.17	0.02	0.00	0.63	0.00	0.45
20.00%	11	1	2	After 3rd	100	0.02	0.11	0.02	0.00	0.56	0.00	0.44
20.00%	11	1	4	Before	30	0.07	8.87	0.03	0.00	0.29	0.00	0.29
20.00%	11	1	4	After 1st	27	0.02	0.32	0.03	0.00	0.78	0.00	0.57
20.00%	11	1	4	After 2nd	24	0.01	0.11	0.02	0.00	0.63	0.00	0.46
20.00%	11	1	4	After 3rd	120	0.01	0.11	0.02	0.00	0.64	0.00	0.50
20.00%	10	1	4	Before	30	0.28	10.00	0.00	0.00	1.13	0.00	0.84
20.00%	10	1	4	After 1st	30	0.24	2.37	0.00	0.00	2.22	0.00	1.07
20.00%	10	1	4	After 2nd	30	0.26	2.17	0.00	0.00	1.92	0.00	1.05
20.00%	10	1	4	After 3rd	120	0.19	1.13	0.00	0.00	1.96	0.00	1.06
10.00%	10	1	4	Before	30	0.27	10.14	0.01	0.00	1.20	0.00	0.84
10.00%	10	1	4	After 1st	26	0.28	5.06	0.00	0.00	2.00	0.00	1.08
10.00%	10	1	4	After 2nd	23	0.27	3.71	0.00	0.00	2.11	0.00	1.07
10.00%	10	1	4	After 3rd	120	0.27	3.36	0.00	0.00	1.88	0.00	1.03
10.00%	11	1	4	Before	30	0.09	8.73	0.03	0.00	0.30	0.00	0.44
10.00%	11	1	4	After 1st	27	0.06	0.71	0.02	0.00	0.76	0.00	0.49
10.00%	11	1	4	After 2nd	23.5	0.05	0.39	0.02	0.00	0.63	0.00	0.46

						Concentration [g/L]						
lix conc	**pH**	**A**	**O**	**PLS**	**vol [mL]**	**Al**	**Cu**	**Fe**	**Ni**	**Pb**	**Sn**	**Zn**
10.00%	11	1	4	After 3rd	120	0.11	0.28	0.04	0.00	0.56	0.00	0.44

Table B.4: Solvent extraction AAS data

LIX-84I conc	pH	A	O	Sample	Actual Conc [g/L]	phase vol [mL]	mass in phase [g]
5%	10	1	1	PLS before	18.71	100	1.87
5%	10	1	1	PLS after	14.58	100	1.46
5%	10	1	1	H2SO4	2.79	100	0.28
10%	10	1	1	PLS before	17.38	100	1.74
10%	10	1	1	PLS after	13.60	100	1.36
10%	10	1	1	H2SO4	4.50	100	0.45
15%	10	1	1	PLS before	15.92	100	1.59
15%	10	1	1	PLS after	13.06	100	1.31
15%	10	1	1	H2SO4	9.64	100	0.96
5%	10	1	1	PLS before	18.25	100	1.82
5%	10	1	1	PLS after	15.01	100	1.50
5%	10	1	1	H2SO4	2.53	100	0.25
10%	10	1	1	PLS before	18.03	100	1.80
10%	10	1	1	PLS after	11.88	100	1.19
10%	10	1	1	H2SO4	6.10	100	0.61
15%	10	1	1	PLS before	18.39	100	1.84
15%	10	1	1	PLS after	9.78	100	0.98
15%	10	1	1	H2SO4	9.32	100	0.93
36%	10	1	1	PLS before	13.41	100	1.34
36%	10	1	1	PLS after	3.53	100	0.35
36%	10	1	1	H2SO4	6.49	100	0.65
18%	10	1	2	PLS before	12.98	50	0.65
18%	10	1	2	PLS after	5.58	100	0.56
18%	10	1	2	H2SO4	3.85	100	0.38
12%	10	1	3	PLS before	12.97	50	0.65
12%	10	1	3	PLS after	6.39	50	0.32
12%	10	1	3	H2SO4	1.55	150	0.23
9%	10	1	4	PLS before	12.58	50	0.63
9%	10	1	4	PLS after	7.45	50	0.37
9%	10	1	4	H2SO4	0.58	200	0.12
5%	8	1	1	PLS before	1.89	75	0.14
5%	8	1	1	PLS after	1.32	75	0.10
5%	8	1	1	H2SO4	0.45	75	0.03
5%	8	1	2	PLS before	2.02	50	0.10
5%	8	1	2	PLS after	1.30	50	0.07
5%	8	1	2	H2SO4	0.30	100	0.03

LIX-84I conc	pH	A	O	Sample	Actual Conc [g/L]	phase vol [mL]	mass in phase [g]
5%	8	1	4	PLS before	1.80	30	0.05
5%	8	1	4	PLS after	0.71	30	0.02
5%	8	1	4	H2SO4	0.24	120	0.03
5%	10	1	1	PLS before	12.59	75	0.94
5%	10	1	1	PLS after	10.43	75	0.78
5%	10	1	1	H2SO4	2.28	75	0.17
5%	10	1	2	PLS before	13.58	50	0.68
5%	10	1	2	PLS after	9.05	50	0.45
5%	10	1	2	H2SO4	1.80	100	0.18
5%	10	1	4	PLS before	12.54	30	0.38
5%	10	1	4	PLS after	7.10	30	0.21
5%	10	1	4	H2SO4	0.60	120	0.07
10%	8	1	1	PLS before	2.17	75	0.16
10%	8	1	1	PLS after	1.16	75	0.09
10%	8	1	1	H2SO4	0.62	75	0.05
10%	8	1	2	PLS before	2.02	50	0.10
10%	8	1	2	PLS after	0.03	50	0.00
10%	8	1	2	H2SO4	0.15	100	0.02
10%	8	1	4	PLS before	1.70	30	0.05
10%	8	1	4	PLS after	0.09	30	0.00
10%	8	1	4	H2SO4	0.35	120	0.04
10%	10	1	1	PLS before	12.03	75	0.90
10%	10	1	1	PLS after	7.86	75	0.59
10%	10	1	1	H2SO4	4.48	75	0.34
10%	10	1	2	PLS before	14.36	50	0.72
10%	10	1	2	PLS after	5.85	50	0.29
10%	10	1	2	H2SO4	2.36	100	0.24
10%	10	1	4	PLS before	13.24	30	0.40
10%	10	1	4	PLS after	8.21	30	0.25
10%	10	1	4	H2SO4	0.82	120	0.10
20%	8	1	1	PLS before	2.23	75	0.17
20%	8	1	1	PLS after	0.58	75	0.04
20%	8	1	1	H2SO4	1.38	75	0.10
20%	8	1	2	PLS before	2.00	50	0.10
20%	8	1	2	PLS after	0.15	50	0.01
20%	8	1	2	H2SO4	0.59	100	0.06
20%	8	1	4	PLS before	1.99	30	0.06
20%	8	1	4	PLS after	0.09	30	0.00
20%	8	1	4	H2SO4	0.53	120	0.06
20%	10	1	1	PLS before	12.80	75	0.96
20%	10	1	1	PLS after	5.67	75	0.43
20%	10	1	1	H2SO4	6.63	75	0.50
20%	10	1	2	PLS before	11.79	50	0.59

LIX-84I conc	pH	A	O	Sample	Actual Conc [g/L]	phase vol [mL]	mass in phase [g]
20%	10	1	2	PLS after	4.79	50	0.24
20%	10	1	2	H2SO4	3.06	100	0.31
20%	10	1	4	PLS before	12.02	30	0.36
20%	10	1	4	PLS after	4.39	30	0.13
20%	10	1	4	H2SO4	1.26	120	0.15
5%	10	1	1	PLS before	10.03	50	0.50
5%	10	1	1	PLS after	8.29	50	0.41
5%	10	1	1	H2SO4	1.79	50	0.09
5%	10	1	1	PLS before	8.29	47	0.39
5%	10	1	1	PLS after	6.03	47	0.28
5%	10	1	1	H2SO4	2.03	50	0.10
5%	10	1	1	PLS before	6.03	43	0.26
5%	10	1	1	PLS after	5.41	43	0.23
5%	10	1	1	H2SO4	1.07	50	0.05
5%	10	1	2	PLS before	10.59	50	0.53
5%	10	1	2	PLS after	6.78	50	0.34
5%	10	1	2	H2SO4	1.55	100	0.15
5%	10	1	2	PLS before	6.78	46	0.31
5%	10	1	2	PLS after	4.35	46	0.20
5%	10	1	2	H2SO4	1.24	100	0.12
5%	10	1	2	PLS before	4.35	42	0.18
5%	10	1	2	PLS after	3.51	42	0.15
5%	10	1	2	H2SO4	0.37	100	0.04
5%	10	1	4	PLS before	10.29	30	0.31
5%	10	1	4	PLS after	4.90	30	0.15
5%	10	1	4	H2SO4	1.26	120	0.15
5%	10	1	4	PLS before	4.90	27	0.13
5%	10	1	4	PLS after	3.81	27	0.10
5%	10	1	4	H2SO4	0.31	120	0.04
5%	10	1	4	PLS before	3.81	23	0.09
5%	10	1	4	PLS after	3.59	23	0.08
5%	10	1	4	H2SO4	0.06	120	0.01
10%	10	1	1	PLS before	10.17	50	0.51
10%	10	1	1	PLS after	6.19	50	0.31
10%	10	1	1	H2SO4	4.17	50	0.21
10%	10	1	1	PLS before	6.19	46	0.28
10%	10	1	1	PLS after	4.38	46	0.20
10%	10	1	1	H2SO4	1.54	50	0.08
10%	10	1	1	PLS before	4.38	43	0.19
10%	10	1	1	PLS after	3.75	43	0.16
10%	10	1	1	H2SO4	0.39	50	0.02
10%	10	1	2	PLS before	10.73	50	0.54
10%	10	1	2	PLS after	4.72	50	0.24

LIX-84I conc	pH	A	O	Sample	Actual Conc [g/L]	phase vol [mL]	mass in phase [g]
10%	10	1	2	H2SO4	2.92	100	0.29
10%	10	1	2	PLS before	4.72	46	0.22
10%	10	1	2	PLS after	3.49	46	0.16
10%	10	1	2	H2SO4	0.54	100	0.05
10%	10	1	2	PLS before	3.49	43	0.15
10%	10	1	2	PLS after	2.83	43	0.12
10%	10	1	2	H2SO4	0.26	100	0.03
10%	10	1	4	PLS before	10.67	30	0.32
10%	10	1	4	PLS after	5.11	30	0.15
10%	10	1	4	H2SO4	1.29	120	0.15
10%	10	1	4	PLS before	5.11	26	0.13
10%	10	1	4	PLS after	3.63	26	0.09
10%	10	1	4	H2SO4	0.34	120	0.04
10%	10	1	4	PLS before	3.63	23	0.08
10%	10	1	4	PLS after	3.56	23	0.08
10%	10	1	4	H2SO4	0.08	120	0.01
20%	10	1	1	PLS before	10.48	50	0.52
20%	10	1	1	PLS after	3.74	50	0.19
20%	10	1	1	H2SO4	4.57	50	0.23
20%	10	1	1	PLS before	3.74	46	0.17
20%	10	1	1	PLS after	3.03	46	0.14
20%	10	1	1	H2SO4	1.33	50	0.07
20%	10	1	1	PLS before	3.03	43	0.13
20%	10	1	1	PLS after	2.26	43	0.10
20%	10	1	1	H2SO4	0.41	50	0.02
20%	10	1	2	PLS before	10.70	50	0.53
20%	10	1	2	PLS after	4.32	50	0.22
20%	10	1	2	H2SO4	3.09	100	0.31
20%	10	1	2	PLS before	4.32	47	0.20
20%	10	1	2	PLS after	2.78	47	0.13
20%	10	1	2	H2SO4	0.63	100	0.06
20%	10	1	2	PLS before	2.78	44	0.12
20%	10	1	2	PLS after	2.35	44	0.10
20%	10	1	2	H2SO4	0.22	100	0.02
20%	10	1	4	PLS before	11.15	30	0.33
20%	10	1	4	PLS after	3.52	30	0.11
20%	10	1	4	H2SO4	1.63	120	0.20
20%	10	1	4	PLS before	3.52	27	0.09
20%	10	1	4	PLS after	2.55	27	0.07
20%	10	1	4	H2SO4	0.22	120	0.03
20%	10	1	4	PLS before	2.55	24	0.06
20%	10	1	4	PLS after	2.41	24	0.06
20%	10	1	4	H2SO4	0.03	120	0.00

APPENDIX C SOLVENT AND RESINS DATA SHEETS

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BASF
We create chemistry

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LIX® 84-I

Solvent Extraction Reagent

Description

LIX 84-I solvent extraction reagent is water insoluble 2-hydroxy-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent.

Principal uses

LIX 84-I forms water insoluble complexes with various metallic cations in a manner similar to that shown below for copper:

$$2RH_{(org)} + Cu^{+2}_{(aq)} \rightleftharpoons R_2Cu_{(org)} + 2H^{+}_{(aq)}$$

Copper extraction from typical leach solutions is pH dependent. Stripping is accomplished with acid solutions such as a typical barren electrolyte from copper electrowinning.

Typical properties

Physical form	Fluid amber liquid
Specific gravity (25 °/25 °C)	0.89 – 0.91 g/cm³
Flash point[1]	Greater than 160 °F
Copper complex solubility	> 30 g/l Cu at 25 °C

[1] Flash point is determined by Setaflash closed cup.

Performance specifications[2]

Maximum copper loading	4.7 to 5.0 g/l Cu
Extraction isotherm point	≥ 3.65 g/l Cu
Extraction kinetics	≥ 90 % (60 seconds)
Extraction Cu/Fe selectivity	≥ 2000
Extraction phase separation	≤ 60 seconds
Strip isotherm point	≤ 0.50 g/l Cu
Net copper transfer	≥ 3.30 g/l Cu
Strip kinetics	≥ 90 % (30 seconds)
Strip phase separation	≤ 80 seconds

[2] Performance parameters are determined using the Standard Quality Control Test of LIX Reagents

Storage & Shelf life

LIX 84-I is stable for at least five years from date of manufacture in its unopened, original packaging.

Shipping

LIX 84-I is supplied in 15 kg jerrican,182 kg drum or 900 kg IBC.

Technical service

Advice and assistance in the running of laboratory and plant tests is given by representatives of BASF, who are experienced in mineral processing applications.

Health & Safety

Please refer to the Safety Data Sheet for detailed information concerning product's hazards and appropriate protective measures in the workplace.

Note

The data contained in this publication are based on our current knowledge and experience. In view of the many factors that may affect processing and application of our product, these data do not relieve processors from carrying out their own investigations and tests; neither do these data imply any guarantee of certain properties, nor the suitability of the product for a specific purpose. Any descriptions, drawings, photographs, data, proportions, weights etc. given herein may change without prior information and do not constitute the agreed contractual quality of the product. It is the responsibility of the recipient of our products to ensure that any proprietary rights and existing laws and legislation are observed.

December 2015

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PRODUCT DATASHEET

Purolite®
S930Plus

Polystyrenic Macroporous Iminodiacetic acid Chelating Resin, High Capacity

PRINCIPAL APPLICATIONS

- Brine Decalcification

ADVANTAGES

- High operating capacity
- Excellent osmotic stability

SYSTEMS

- Acidic liquors and pulps

TYPICAL PACKAGING

- 1 ft³ Sack
- 25 L Sack
- 5 ft³ Drum (Fiber)
- 1 m³ Supersack
- 42 ft³ Supersack

TYPICAL PHYSICAL & CHEMICAL CHARACTERISTICS:

Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical Beads
Functional Group	Iminodiacetic
Ionic Form	Na^+ form
Copper Capacity (min.)	50 g/L
Moisture Retention	52 - 60 % (Na^+ form)
Particle Size Range	425 - 1000 µm
< 425 µm (max.)	2 %
Uniformity Coefficient (max.)	1.5
Reversible Swelling, $H^+ \rightarrow Na^+$ (max.)	35 %
Specific Gravity	1.18
Shipping Weight (approx.)	750 - 800 g/L (46.9 - 50.0 lb/ft³)
Temperature Limit	80 °C (176.0 °F)

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PRODUCT INFORMATION
LEWATIT® TP 207

Lewatit®

Lewatit® TP 207 is a weakly acidic, macroporous cation exchange resin with chelating iminodiacetate groups for the selective extraction of heavy metal cations from weakly acidic to weakly basic solutions. Divalent cations are removed from neutralized waters in the following order:
Copper > Vanadium (VO^{2+}) > Uranium (UO_2^{2+}) > Lead > Nickel > Zinc > Cadmium > Iron(II) > Beryllium > Manganese > Calcium > Magnesium > Strontium > Barium >>> Sodium.

It is especially suitable for use in the following applications:

- selective removal of trace heavy metals from effluents of the metal surface finishing industry, even in the presence of high calcium concentrations
- recovery of useful metals from electroplating rinse waters
- removal of metal contaminants from processing baths
- concentration, extraction and recovery of heavy metals from hydrometallurgical solutions
- removal of heavy metals from contaminated ground water for the purpose of potable water production or ground water remediation.

The selective extraction is achieved even in the presence of the following complexing agents:

- nitrogen compounds, e.g. ammonia, aliphatic and aromatic amines
- multivalent carboxylic acids, e.g. citric acid, gluconic acid, glucuronic acid, oxalic acid, tartaric acid
- phosphates, e.g. tetrasodium diphosphate, sodium polyphosphate.

Lewatit® TP 207 does not remove heavy metals from solutions containing EDTA or NTA respectively. Only cadmium is removed from solutions containing cyanides. For the extraction of those heavy metals which follow the uranyl oxide ion in the selectivity sequence as shown above, **Lewatit® TP 207** has to be conditioned with caustic soda solution after every regeneration cycle before every exhaustion cycle. After the conditioning it is partially in a salt-form, e.g. mono-sodium-form.

The special properties of this product can only be fully utilized if the technolgy and process used correspond to the current state-of-the-art and the operating conditions are adapted to the individual requirements. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

General Description

Ionic form as shipped	Na^+
Functional group	iminodiacetic acid
Matrix	crosslinked polystyrene
Structure	macroporous
Appearance	beige, opaque

Physical and Chemical Properties

		metric units	
Total capacity*	H-Form	min. eq/l	2.2
Uniformity Coefficient*		max.	1.7
Bead size*	> 90 %	mm	0.4 - 1.25
Effective size*		mm	0.55 (+/- 0.05)
Specific pressure drop	(15 °C)	approx. kPa*h/m²	1.1
Bed expansion	(20 °C, per m/h)	approx. vol. %	4
Bulk density	(+/- 5 %)	g/l	720
Density		approx. g/ml	1.17
Water retention		wt. %	53 - 58
Volume change	Na^+ --> H^+	max. vol. %	-30
Stability	at pH-range		0 - 14
Storability	of the product	max. years	2
Storability	temperature range	°C	-20 - 40

* Specification values subjected to continuous monitoring.

Recommended Operating Conditions*

		metric units	
Operating temperature		max. °C	80
Operating pH-range			1.5 - 9
Bed depth		min. mm	1000
Pressure drop		max. kPa	250
Specific velocity	operation	max. BV/h	30
Bed expension	backwash	min. %	40
Linear velocity	operation	max. m/h	40
Linear velocity	backwash (20 °C)	approx. m/h	10
Freeboard	backwash (extern / intern)	vol. %	80
Regenerant			HCl H_2SO_4 HNO_3
Co current regeneration	level	approx. g/l	HCl 150 H_2SO_4 200 HNO_3 250
Co current regeneration	concentration	approx. wt. %	HCl 7.5 H_2SO_4 10 HNO_3 12
Linear velocity	regeneration	approx. m/h	5
Linear velocity	rinsing	approx. m/h	5
Conditioning			NaOH Mono-Na Di-Na
Conditioning	level	g/l	40 - 48 80 - 96
Conditioning	concentration	approx. wt. %	4
Linear velocity	conditioning	approx. m/h	5
Linear velocity	regeneration	approx. m/h	5
Linear velocity	rinsing	approx. m/h	5
Rinse water requirement		approx. BV	5

The recommended operating conditions refer to the use of the product under normal operating conditions. It is based on tests in pilot plants and data obtained from industrial applications. However, additional data are needed to calculate the resin volumes required for industrial scale ion exchange units. These can be found in our technical data sheets, have to be requested from Lanxess-application-specialists or have to be elaborated in laboratory- and pilot-tests.

Additional Information & Regulations

Safety precautions

Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

Toxicity

The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

Disposal

In the European Community Ion exchange resins have to be disposed, according to the European waste nomenclature which can be accessed on the internet-site of the European Union.

Storage

It is recommended to store ion exchange resins at temperatures above the freezing point of water under roof in dry conditions without exposure to direct sunlight. If resin should become frozen, it should not be mechanically handled and left to thaw out gradually at ambient temperature. It must be completely thawed before handling or use. No attempt should be made to accelerate the thawing process.

PRODUCT INFORMATION
LEWATIT® MonoPlus TP 220

Lewatit®

Lewatit® MonoPlus TP 220 is a macroporous weakly basic resin with chelating bispicolylamine groups for copper, nickel and cobalt processing solutions.

Lewatit® MonoPlus TP 220 is of monodispersed bead size distribution, means beads of uniform size. The resin is characterized by high kinetics leading to a good utilization of the available capacity combined with a high mechanical and osmotic stability.

Lewatit® MonoPlus TP 220 is capable of selectively capturing transition metal ions from acidic solutions with pH less than 2, or in the presence of strong chelating agents. Therefore it is in particular suitable for the use in the following application:

- Cobalt electrolyte purification (Cobalt/Nickel separation)
- Separation of nickel from a chromium (III) or ferric solution
- Copper removal from strongly acidic solutions (pH < 2)

Lewatit MonoPlus TP 220 is delivered in the fully protonated form by sulphuric acid which means that the resin is fully swollen and hydrated. Therefore, it can be used without further treatment.

The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the-art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

PRODUCT INFORMATION
LEWATIT® MonoPlus TP 220

Lewatit®

General Description

Ionic form as shipped	fully protonated
Form	weak base
Type	chelating resin
Functional group	bis-picolylamine
Matrix	crosslinked polystyrene
Structure	macroporous
Appearance	opaque

Physical and Chemical Properties

		metric units	
Copper loading	pH = 1,4; 5 g/L feed	g/l	min. 29
Uniformity Coefficient*		max.	1.1
Mean bead size*		mm	0.62(+/- 0.05)
Bulk density	(+/- 5 %)	g/l	690
Density		approx. g/ml	1.1
Water retention		wt. %	48 - 60
Storability	of the product	max. years	2
Storability	temperature range	℃	-20 - 40

* Specification values subjected to continuous monitoring.

Additional Information & Regulations

Safety precautions

Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

Toxicity

The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

Disposal

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